Trennung von Metalkomplexisomerien mit Ionenaustauscher. II. Über Dichloro-bis-äthylendiamin-kobalt (III)- und Dirhodanato-bis-äthylendiamin-kobalt (III)-ionen*

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(Eingegangen am 30. April 1956)

Wir forschten in diesem Versuche das Verhalten der Komplexisomerie gegen Ionenaustauscher und ihre Trennung auszuführen. Wir veröffentlichten schon über sogenannte Flavo- und Croseo-kobaltsalze[1] und berichten hier über *cis*-, *trans*-Dichloro-bis-athylendiamin-kobalt (III)-chlorid und *cis*-, *trans*-Dirhodanato-bis-athylendiamin-kobalt (III)-chlorid.

Experimenteller Teil

Herstellung von Komplexsalzen.—*cis*-, *trans*-$[Coen_2Cl_2]Cl$ und *trans*-$[Coen_2(CNS)_2]Cl$ wurden nach der Literatur[2] dargestellt, während *cis*-$[Coen_2(CNS)_2]Cl$ auf unsere Weise hergestellt wurde.

Fünf Gramme $[Coen_2CO_3]Cl \cdot H_2O$ wurden in Wasser von 50 ccm gelöst und darin 4 g KCNS zugegeben. Nachdem das Gemisch mit Essigsäure angesäuert wurde, wurde es konzentriert, um das rohe Salz zu gewinnen. Die Reinigung geschah durch Lösen in verd. Salzsäure und dann noch einmal in Wasser.

Wir vergewisserten uns, dass alle diese Komplexsalze durch Messung ihrer Absorptionsspektra unvermischt sind. Die Salzlösungen wurden zu einer etwa 10^{-2} M Konzentration zubereitet und als Probelösungen gebraucht.

Durchführung der Elutionsversuche.—Als Austauschmaterial war der Kationenaustauscher Amberlit IR 120 in der Na-Form verwendet. Neun Gramme davon wurden mit Wasser in eine Säule von 1.5 cm Durchmesser und 30 cm Höhe eingefüllt. Je 5 cm der oben gezeigten Probelösung wurden darauf einzeln oder gemischt gegeben. Nachdem die Säule mit Wasser genug gewaschen wurde, wurde 0.5 M Natriumchloridlösung (f = 1.012) weiter als Eluierungsmittel eingegossen. Die ausfliessende Lösung, die eine Durchflussgeschwindigkeit von 1 ccm in 3.5 Minuten einhält, wurde je 10 cm mit Hilfe von automatischem Fraktionierkollektor gesammelt.

Die Erkennung von *cis*- oder *trans*-Ionen wurde bei ihren Maximalwellenlängen durch Messung der Extinktion von einzelner Fraktion ausgeführt. D. h. die Wellenlängen 535 mμ und 615 mμ sind zur Unterscheidung der *cis*-, *trans*-$[Coen_2Cl_2]^+$, und die 490 mμ und 505 mμ zu der von *cis*-, *trans*-$[Coen_2(CNS)_2]^+$ benutzt worden.

Messungen der Adsorptionsmenge von Komplexionen an Austauschern.—Zwanzig Kubikzentimeter der von 10^{-2} M zu 10^{-1} M präparierten Lösung wurden in die Erlenmeyerflasche, worin 100 mg Austauscher sind, eingeleitet. Sie wurde drei Stunden im auf 25°C gehaltenen Thermostat gestellt und oft gerührt. Die Lösung wurde vom Adsorbense abgetrennt und ihre Extinktion bei Maximalwellenlänge gemessen. Die Extinktion der ohne Adsorbens gestellten Lösung wurde auch gleich gemessen. Durch die Differenz von beiden Extinktionen rechnete man die Adsorptionsmenge im mM an 100 mg Austauscher.

Zu den alleinigen Lichtabsorptionsmessungen wurde Beckman DU Typus Spektrophotometer mit der 1.00 cm Küvette benutzt.

Ergebnisse

Tabelle I und Abb. 1 zeigen das Ergebnis, das nach der obigen Weise infolge der Trennung der gemischten Lösung von *cis*-, *trans*-$[Coen_2Cl_2]^+$ gewonnen wurde. Bei der einzelnen Lösung sowohl als auch der Gemischten strömte jedes Komplexion mit dem gleichen Verhältnis aus.

Es begann nämlich das *trans*-Ion in der Fraktionsnummer 6 zu erscheinen und zeigte das Konzentrationsmaximum in der Nummer 7, wurde aber in der Nummer 10 kaum nachgewiesen. Das *cis*-Ion begann in der Nummer 10 zu erscheinen und zeigte das Maximum in der Nr. 12.

Die gleiche Erscheinung wurde auch über *cis*-, *trans*-$[Coen_2(CNS)_2]^+$ beobachtet (Siehe Tabelle II und Abb. 2). Bei dem *trans*-Ion erscheint das Maximum der Konzentrationsverteilung in der Nr. 5, bei dem *cis*-Ion in der Nr. 14. Es wurde beobachtet, dass dieses Ion im ganzen langsam ausströmt. Das *cis*-Ion strömte mit voller Wirkung als 2 M Natriumchlorid Lösung statt der 0.5 M Lösung abgetropft wurde, sofort nachdem das *trans*-Ion fast schloss.

Tabelle III und Abb. 3 zeigen das Ergebnis der Trennung von *cis*-, *trans*-$[Coen_2(NO_2)_2]^+$. Wir versuchten schon mit Austauscher von NH_4-Form über dieselben[1], aber wir wieder holten es um ihre Trennung zu vergleichen. Das *trans*- Ion zeigt hier in der Fraktionsnummer 6 seine maximale Verteilung und *cis*-Ion in der Nr. 17.

* Dies wurde auf der 9ten Generalversammlung der Chemischen Gesellschaft vou Japan vorgetragen, am 2. April, 1956, in Kyoto.

1) M. Mori, M. Shibata und J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955).

2) T. Inoue, "Synthetische anorganische Chemie (Mukikagaku-Seizo-Jikken)", Shokabo, Tokyo, 1946.

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TABELLE I

TRENNUNG EINES GEMISCHES VON *cis*- UND *trans*-$[Coen_2Cl_2]^+$

Fraktion Nr.	E_{535}	E_{615}	E_{615}/E_{535}
5	0	0	—
6	0.010	0.056	5.60
7	0.030	0.166	5.53
8	0.030	0.165	5.50
9	0.016	0.084	5.25
10	0.050	0.024	0.48
11	0.114	0.039	0.37
12	0.155	0.047	0.30
13	0.133	0.040	0.30
14	0.087	0.029	0.33
15	0.048	0.015	0.31
16	0.030	0.010	0.33
17	0.019	0.006	0.31
18	0.008	0.003	0.37

TABELLE II

TRENNUNG EINES GEMISCHES VON *cis*- UND *trans*-$[Coen_2(CNS)_2]^+$

Fraktion Nr.	E_{490}	E_{505}	E_{505}/E_{490}
2	0	0	—
3	0.031	0.036	1.16
4	0.200	0.229	1.15
5	0.362	0.410	1.13
6	0.328	0.370	1.13
7	0.216	0.246	1.14
8	0.123	0.138	1.12
9	0.076	0.086	1.13
10	0.051	0.050	1.02
11	0.100	0.090	0.90
12	0.125	0.112	0.89
13	0.132	0.119	0.90
14	0.140	0.125	0.89
15	0.135	0.122	0.90
16	0.130	0.114	0.88
17	0.120	0.106	0.88
18	0.109	0.100	0.91
19	0.082	0.073	0.89
20	0.072	0.063	0.87
21	0.065	0.060	0.92
22	0.056	0.050	0.89
23	0.037	0.034	0.91
24	0.020	0.018	0.90
25	0.009	0.008	0.88

TABELLE III

TRENNUNG EINES GEMISCHES VON *cis*- UND *trans*-$[Coen_2(NO_2)_2]^+$

Fraktion Nr.	E_{324}	E_{340}	E_{340}/E_{324}
3	0	0	—
4	0.149	0.190	1.28
5	2.519	3.245	1.29
6	6.468	8.360	1.29
7	4.455	5.742	1.29
8	1.276	1.606	1.26
9	0.216	0.269	1.25
10	0.100	0.125	1.25
11	0.092	0.090	0.97
12	0.342	0.265	0.77
13	1.034	0.803	0.77
14	2.090	1.595	0.76
15	3.432	2.640	0.76
16	3.938	3.003	0.76
17	3.982	3.025	0.76
18	3.377	2.574	0.76
19	2.970	2.255	0.75
20	1.980	1.540	0.77
21	1.463	1.122	0.76
22	0.815	0.633	0.77
23	0.513	0.395	0.76
24	0.268	0.206	0.76
25	0.125	0.095	0.76
26	0.055	0.043	0.78

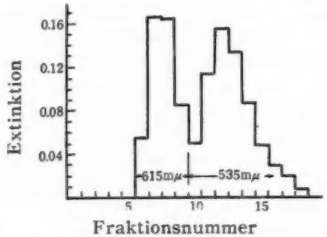

Abb. 1. Trennung eines Gemisches von *cis*-und *trans*-$[Coen_2Cl_2]^+$.

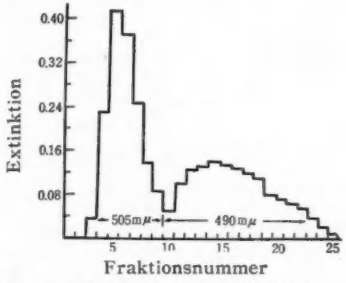

Abb. 2. Trennung eines Gemisches von *cis*-und *trans*-$[Coen_2(CNS)_2]^+$.

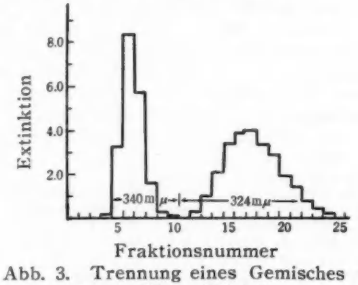

Abb. 3. Trennung eines Gemisches von *cis*-und *trans*-$[Coen_2(NO_2)_2]^+$.

Die über Adsorption der Komplexionen an Austauscher gewonenen Ergebnisse werden in Tabellen IV und V gezeigt. Hierbei bezeichnet C_o die Anfangskonzentration, C_s die Gleichgewichtskonzentration der Komplexionen, m die Menge des Austauschers und C_r die adsorbierte Menge an 100 mg Austauscher. K_d ist der nachstehend definierte Verteilungskoeffizient.

$$K_d = \frac{\text{adsorbierte Menge (mM) pro 1 meq. } H^+\text{-wertiger Austauscher (250 mg)}}{\text{Gleichgewichtskonzentration (mM/l)}}$$

$$= \frac{C_r}{C_s} \times 2.50$$

Diese Ergebnisse werden auch in Abb. 4 graphish zusammengestellt. Auf der Abszisse wird die Gleichgewichtskonzentration und auf der Ordinate der Verteilungskoeffizient logarithmisch aufgetragen.

TABELLE IV

ADSORPTION VON *cis*- UND *trans*-$[Coen_2(CNS)_2]Cl$ AN AUSTAUSCHER (250 mg Austauscher, 1 meq. H^+)

C_o (mM/l)	C_s (mM/l)	C_r (mM/100 mg)	m (mg)	K_d	E_{505}/E_{490}
cis-					
7.66	0.95	0.064	209.4	0.16	0.90
3.06	0.49	0.050	103.0	0.26	0.88
1.55	0.19	0.027	101.1	0.35	0.90
0.77	0.09	0.013	101.5	0.36	0.86
0.15	0.02	0.003	100.8	0.37	0.85
trans-					
10.16	2.23	0.078	203.9	0.08	1.14
4.06	1.10	0.057	103.9	0.12	1.13
2.03	0.47	0.031	100.7	0.16	1.14
1.02	0.23	0.015	100.4	0.16	1.14
0.20	0.04	0.003	102.6	0.18	1.09

TABELLE V

ADSORPTION VON *cis*- UND *trans*-$[Coen_2(NO_2)_2]Cl$ AN AUSTAUSCHER

C_o (mM/l)	C_s (mM/l)	C_r (mM/100 mg)	m (mg)	K_d	E_{340}/E_{324}
cis-					
10.44	0.93	0.092	206.5	0.24	0.74
4.18	0.53	0.073	100.4	0.34	0.76
2.09	0.24	0.037	100.9	0.38	0.75
1.04	0.10	0.018	101.2	0.45	0.76
0.42	0.04	0.007	101.0	0.43	0.75
trans-					
10.80	2.37	0.083	203.8	0.08	1.25
4.32	1.00	0.065	100.9	0.16	1.27
2.16	0.42	0.033	104.6	0.19	1.21
1.08	0.20	0.018	100.9	0.22	1.23
0.43	0.07	0.007	101.5	0.25	1.26

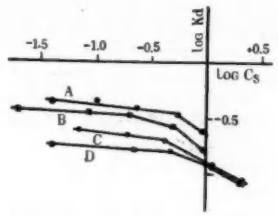

Abb. 4. Adsorption von Komplexionen an Austauscher.
A *cis*-$[Coen_2(NO_2)_2]^+$
B *cis*-$[Coen_2(CNS)_2]^+$
C *trans*-$[Coen_2(NO_2)_2]^+$
D *trans*-$[Coen_2(CNS)_2]^+$

Die über *cis*-, *trans*-$[Coen_2Cl_2]^+$ gemessenen Ergebnisse werden nicht in Abb. 4 zusammengestellt, da diese Komplexe teilweise zu den Aquokomplexe übergingen.

Diskussion

E. L. King und R. R. Walter[3] haben schon gefunden, dass *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ als *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ schneller ausfliessen, und wir[1] bestätigten auch dies über $[Co(NH_3)_4(NO_2)_2]^+$ und $[Coen_2(NO_2)_2]^+$. Aus diesen Tatsachen und den hier gewonnenen Ergebnisses entsteht wahrscheinlich ein empirisches Gesetz, nach dem *trans*-Form als *cis*-Form bei $[CoA_4X_2]^+$ oder $[Co(a\text{-}a)_2X_2]^+$ schneller ausfliesst. Es dünkt uns, dass solcher Unterschied in der Affinität zum Austauscher in dem Unterschiede der von Säureradikal X produzierten Dipolmomenten begründet ist.

Die Affinität zum Austauscher entsteht aus der Differenz von Ligande X sowohl unter denselben *cis*-Formen als auch unter denselben *trans*-Formen. Nach unseren Versuchen nimmt die Affinität zum Austauscher bei *trans*-Formen in der Reihenfolge $[Coen_2Cl_2]^+ > [Coen_2(NO_2)_2]^+ > [Coen_2(CNS)_2]^+$, bei *cis*-Formen $[Coen_2(NO_2)_2]^+ > [Coen_2(CNS)_2]^+ > [Coen_2Cl_2]^+$ ab. Dass die beiden Reihenfolgen nicht übereinstimmen, so meinen wir, ist der Unterschied des herrschenden Faktors zur Affinität. Wir müssen die objektiven Komplexsalze noch mehr vermehren und versuchen, um den Faktor zu erforschen.

Wir stellten oft fest, dass *cis*-, *trans*-Form sich einander in fen hergestellten Komplexsalzen mischen. In solchem Falle kann diese Weise als eine Weise bequem benutzen, die die Reinheit der Komplexsalzen einfach anerkennen kann.

Zusammenfassung

Wir machten Versuche über Trennung von

3) E. L. King und R. R. Walter, *J. Am. Chem. Soc.*, 74, 4471 (1952).

cis- und *trans*-Form der drei Isomerien—$[Coen_2Cl_2]Cl$, $[Coen_2(CNS)_2]Cl$ und $[Coen_2(NO_2)_2]Cl$—, benutzten dabei als Austauscher den Kationenaustauscher Amberlit IR 120 in der Na-Form und als Elutionsmittel die 0.5 M Natriumchlorid Lösung und gewannen somit die folgenden Ergebnisse.

1) *Trans*-Form floss immer als *cis*-Form der entsprechenden Komplexsalze schneller aus und wurde fast ganz unter dieser experimentalen Bedingung getrennt (Durchflussgeschwindigkeit 1 cm/3.5 Min).

2) Unter *trans*-Komplexen ist die leichte Elution die nachstehende Reihenfolge:
$[Coen_2(CNS)_2]^+ > [Coen_2(NO_2)_2]^+ > [Coen_2Cl_2]^+$.

Diese Reihenfolge widerspricht nicht den vom Experiment der Adsorption an Austauscher gewonnenen Ergebnisse. Unter *cis*-Komplexen:
$[Coen_2Cl_2]^+ > [Coen_2(CNS)_2]^+ > [Coen_2(NO_2)_2]^+$.

3) Wenn wir dieses mit der über *cis*-, *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ schon veröffentlichten Ergebnissen betrachten, denken wir, dass *trans*-Form als *cis*-Form bei Isomerien von Typus $[CoA_4X_2]^+$ oder $[Co(a\text{-}a)_2X_2]^+$ schneller ausfliesse.

Für die Unterstützung dieser Arbeit sind wir der Stiftung für synthetische wissenschaftliche Forschung am Unterrichtsministerium zu Dank verpflichtet.

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The Solubility of Silver Bromate in Tetrahydrofuran-Water Mixed Solvents

By Ei KOIZUMI and Hiroshi MIYAMOTO

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Introduction

In the previous reports regarding the investigation of the relation between solubilities of inorganic salt and dielectric constants of solvents, the solubilities of silver bromate in dioxane- and sucrose-water mixed solvents were described[1,2]. In the present work, the solubility of silver bromate in tetrahydrofuran-water mixed solvents which have a wide range of dielectric constant dependent on the composition was measured at 20°, 25° and 30°C. These data were examined using the theoretical formula[3] concerning the solubility of sparingly soluble salt and the dielectric constant of the solvent.

With regard to the investigations which use tetrahydrofuran as the solvent, few reports have appead so far. The physical properties of the tetrahydrofuran-water system have been studied by Erva[4] and Yoshioka et al.[5] Likewise, the solubility of silver bromate in this mixed solvent has not yet been measured.

1) E. Koizumi and H. Miyamoto, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 1302 (1954).
2) E. Koizumi and H. Miyamoto, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **77**, 193 (1956).
3) E. Koizumi, *J. Chem. Soc. Japan*, **68**, 19 (1947).
4) J. Erva, *Suomen Kemistilehti*, **28B**, 131 (1955). —By *C. A.*, **50**, 6171 (1956).
5) T. Yoshioka and M. Taniyama, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **57**, 747 (1954).

Experimental

(1) Preparation of Solute and Solvent.—The silver bromate was prepared from the dilute solution of silver nitrate and potassium bromate by the infinite dilution method. The precipitates were recrystallized from boiling conductivity water by the modified Reedy's method[6], and stocked in the vacuum.

After the inhibitor was removed, the tetrahydrofuran (from Badische Anilin und Sodafabrik A. G.) was purified twice by fractional distillation in a special rectifier with threefold reflux tube (30 cm. in length) and glass spiral (25 cm. in length) in its inner tube. The fraction boiling at 64.5°–65.5°C was used for the present experiment. From the density determination at 25°C using a Sprengel type pycnometer, this fraction was found to have a purity of 99.15% (wt.), when calculated after Critchfield's empirical equation assuming water to be the only impurity. This grade of purity was sufficient for the present purpose.

Eleven tetrahydrofuran-water mixed solvents were prepared from the purified tetrahydrofuran mentioned above and the conductivity water (1×10^{-6} mho at 20°C), the concentrations of which are ranging from zero to 64.232 per cent by weight of tetrahydrofuran.

(2) Determination of the Solubility of Silver Bromate.—The mixed solvent and excess solute were placed in shaking bottles made of quartz, and sealed. The bottles were rotated in thermostats regulated within ±0.02°C of 20°, 25° and 30°C,

6) J. H. Reedy, *J. Am. Chem. Soc.*, **43**, 1440 (1921).

respectively. These bottles were slowly rotated for seventy-two hours, which were sufficient to give the saturated solutions.

The solubility of silver bromate was determined volumetrically from the total silver ion using dichlorofluorescein as the indicator. To the sample to be determined was added a definite excess of sodium chloride solution (0.050 mol./l.), then the sodium chloride remaining was determined by titration with 0.025 mol./l. silver nitrate solution.

Results and Discussions

(1) Results.—The solubilities of silver bromate and other values are shown in Tables I, II, III and IV. The observed solubilities

TABLE I

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 20°C

T. H. F. %(wt.)	Density	Dielectric Constant	Solubility		log S+3	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9982	80.37	7.28	2.62	0.8621	1.244
3.347	0.9966	78.18	6.34	2.35	0.8021	1.279
6.769	0.9952	75.88	5.72	2.18	0.7574	1.318
12.645	0.9936	71.87	4.73	1.89	0.6749	1.391
18.770	0.9909	67.39	3.97	1.68	0.5988	1.484
24.471	0.9880	62.93	3.39	1.51	0.5302	1.589
29.208	0.9853	59.12	2.93	1.37	0.4669	1.691
35.670	0.9801	52.74	2.51	1.26	0.3997	1.896
43.537	0.9719	46.78	1.90	1.05	0.2788	2.138
54.513	0.9595	37.48	1.34	0.85	0.1271	2.668
64.232	0.9461	29.71	0.99	0.73	$\bar{1}$.9956	3.366

TABLE II

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 25°C

T. H. F. %(wt.)	Density	Dielectric Constant	Solubility		log S+3	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9971	78.54	8.59	3.09	0.9340	1.273
3.347	0.9954	76.34	7.62	2.83	0.8820	1.310
6.769	0.9938	74.00	6.83	2.61	0.8344	1.351
12.645	0.9912	69.92	5.81	2.33	0.7642	1.430
18.770	0.9886	65.56	4.88	2.07	0.6884	1.525
24.471	0.9846	61.09	4.23	1.90	0.6263	1.637
29.208	0.9808	57.24	3.67	1.72	0.5647	1.747
35.670	0.9750	50.98	2.90	1.46	0.4624	1.962
43.537	0.9669	45.25	2.31	1.28	0.3636	2.210
54.513	0.9593	36.28	1.53	0.98	0.1847	2.756
64.232	0.9408	28.72	1.13	0.83	0.0531	3.482

TABLE III

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 30°C

T. H. F. %(wt.)	Density	Dielectric Constant	Solubility		log S+3	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9957	76.73	10.02	3.59	1.0009	1.303
3.347	0.9937	74.58	8.99	3.34	0.9538	1.341
6.769	0.9921	72.34	8.08	3.09	0.9074	1.382
12.645	0.9893	68.34	6.82	2.74	0.8338	1.463
18.770	0.9860	63.95	5.62	2.39	0.7497	1.564
24.471	0.9821	59.56	4.79	2.15	0.6803	1.679
29.208	0.9780	55.85	4.12	1.94	0.6149	1.791
35.670	0.9727	49.70	3.28	1.66	0.5159	2.012
43.537	0.9640	44.01	2.55	1.42	0.4065	2.272
54.513	0.9498	35.18	1.77	1.14	0.2480	2.843
64.232	0.9361	28.00	1.43	1.10	0.1553	3.571

TABLE IV
SOLVATION RADIUS OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT

T. H. F. %(wt.)	20°C		25°C		30°C	
	$A\times10^8$	$B\times10^8$	$A\times10^8$	$B\times10^8$	$A\times10^8$	$B\times10^8$
3.347	0.773	0.758	0.789	0.774	0.968	0.956
6.769	0.907	0.895	0.988	0.975	1.024	1.013
12.645	0.994	0.983	1.148	1.141	1.154	1.148
18.770	1.135	1.128	1.251	1.248	1.246	1.242
24.471	1.296	1.294	1.433	1.438	1.400	1.403
29.208	1.165	1.166	1.549	1.559	1.503	1.510
35.670	1.743	1.745	1.755	1.777	1.910	1.932
43.537	1.878	1.899	1.966	1.997	2.265	2.302
54.513	2.354	2.402	2.354	2.405	2.390	2.447
64.232	2.463	2.541	2.949	3.050	3.076	3.208

of silver bromate in tetrahydrofuran-water mixed solvents at 20°, 25° and 30°C are listed in the fourth column ($S\times10^3$ mol./l.) and in the fifth column ($S'\times10^4$ mole fraction) of Table I, II and III, respectively. The probable error of observed solubility is $\pm0.02\times10^{-3}$ mol./l. Further, the observed densities of the tetrahydrofuran-water system are given in the second column of Tables I and III. The densities listed in Table II were obtained by applying Critchfield's experimental equation. The probable error of the observed density is $\pm0.9\times10^{-5}$g./cc. The dielectric constants (D) at 20°, 25° and 30°C are those from the data of Critchfield[7].

(2) The Relation between the Solubility and the Dielectric Constant.—The relation between the solubility (S) and the dielectric constant (D) is shown graphically in Figs. 1 and 2. In Fig. 2, these curves are approximated by straight lines in the region of higher dielectric constant (about 60–80), in the range of concentration smaller than about twenty per cent by weight of tetrahydrofuran, while in the whole range of concentration we can see the smoothly continuous curves.

When the concentration of tetrahydrofuran

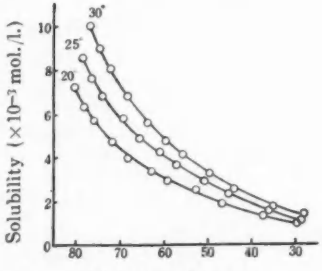

Fig. 1. Relation between solubility and dielectric constant.

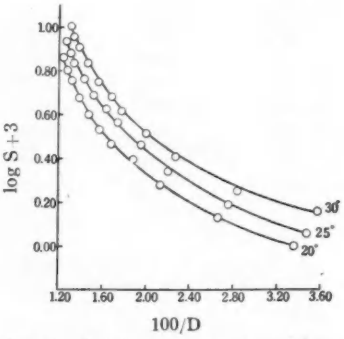

Fig. 2. Relation between logarithm of solubility and reciprocal of dielectric constant.

in solution is relatively low, and provided that the molecular association of the solvent does not exist, the relation between the observed solubility and the dielectric constant of solvent was expressed by the following theoretical equation (I)[3]

$$ln\frac{C_0}{C_1}=\frac{Z^2\varepsilon^2}{2RTr_s}N\left(\frac{1}{D_1}-\frac{1}{D_0}\right)-\frac{Z^2\varepsilon^2}{2kT}\sqrt{\frac{8\pi NZ^2\varepsilon^2}{10^3kT}}\left(\frac{C_1^{\frac{1}{2}}}{D_1^{\frac{3}{2}}}-\frac{C_0^{\frac{1}{2}}}{D_0^{\frac{3}{2}}}\right) \quad (I)$$

where N, R, T, Z, k and ε are the Roschmidt number, gas constant, absolute temperature, valency, Boltzman number, and electric elementary quantum, respectively, C_0 and D_0 are the solubility of the solute in water and the dielectric constant of water, C_1 and D_1 are the solubility of the solute in tetrahydrofuran-water mixed solvents and the dielectric constant of these solvents.

In the equation, as C_0 and D_0 are constant at constant temperature, assuming the solvation radius r_s being constant, neglecting the second term as it is very small compared with the first, the logarithm of solubility of the electrolyte should be reciprocally proportional

7) F. E. Critchfield, J. A. Gibson and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 6044 (1953).

to the dielectric constant. The theoretical equation (I) agrees almost exactly with the experimental results shown in Fig. 2 in the region of higher dielectric constant.

On the other hand, no linear relation was found in the wide range of the dielectric constant of concentrated tetrahydrofuran-water mixed solvents. Undoubtedly, the equation (I) is in such a case incorrect due to the approximations adopted in its theoretical treatment. Since the equation was derived to investigate the relation between the solubility of sparingly soluble salt and the dielectric constant of the solvent, it is not satisfactory for this investigation.

Generally speaking, the solubility of the inorganic salt does not merely depend upon the dielectric constant of the solvent, but it may also depend on the chemical constitution of the solvent. Thus, in a more improved treatment, the intermolecular reaction of the solvent (tetrahydrofuran) and water should be considered. Also to know the effect of polarization of the solubility of inorganic salt in the mixed solvents, the dipole moment of the solvent should be taken into account. Further investigations are necessary in regard to these point.

(3) **Calculation of Solvation Radius.**—The solvation radius (r_s) of silver bromate in these mixed solvents, was calculated by using values of observed solubility. The solvation radius is about 1 Å at each temperature in the solvent of high water concentration. These are listed in Table IV, the values in column (A) were calculated by the equation (I), the values in column (B) by the equation without the second term of the equation (I). The effect of the second term increases with the decrease of the dielectric constant, in a non-linear range of curve in Fig. 2. The solvation radius of this solvent is smaller than in the case of any other previous reports[1,2].

Summary

To investigate the relation between the solubility of inorganic salts and the dielectric constants of solvents, the solubility of silver bromate in tetrahydrofuran-water mixed solvent was determined at 20°, 25° and 30°C, respectively. The logarithm of solubility is almost reciprocally proportional to the dielectric constant of the solvent in the region of the higher dielectric constant. But no linear relation was found in that of the lower dielectric constant of tetrahydrofuran-water mixed solvent.

Also, the solvation radius of silver bromate was calculated applying the above-mentioned data. The solvation radius is about 1 Å at each temperature.

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Hydroformylation and Hydrogenation of Methylacrylate in Presence of Dicobalt Octacarbonyl or Iron Pentacarbonyl. Dependence of Reaction Rate on Partial Pressures of Carbon Monoxide and Hydrogen

By Hiroshi UCHIDA and Kenichiro BANDO

(Received July 26, 1956)

Introduction

In the presence of dicobalt octacarbonyl, ethylacrylate can readily be hydroformylated to β-carbethoxypropionaldehyde. The reaction was once investigated by H. Adkins et al.[1] and thereafter in greater detail by K. Ohashi et al.[2] More recently G. Natta[3] made a study on the hydroformylation of cyclohexene and obtained the remarkable result that the ratio of carbon monoxide to hydrogen in a gas mixture has a considerable influence upon the reaction rate. In this study the hydroformylation of methylacrylate has therefore been conducted by paying special attention to the effect of the gas composition on the rate.

In contrast to dicobalt octacarbonyl, iron pentacarbonyl was generally thought to be ineffective for the hydroformylation. Recently the effect of iron pentacarbonyl upon the isomerization of olefin due to the migration of a double bond-effect which is similar to that of dicobalt octacarbonyl, was however

1) H. Adkins and G. Kresek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).
2) K. Ohashi and S. Suzuki, *J. Chem. Soc. Japan (Ind. Chem. Sec.)*, **56**, 792 (1952), (in Japanese).
3) G. Natta, *Brennstoff-Chem.*, **36**, 176 (1955).

found by A. Asinger et al.[4], so far as the carbon monoxide pressure was comparatively low. The present paper also deals with the reaction that has been made between methylacrylate and gaseous mixtures comprising carbon monoxide and hydrogen in the presence of iron pentacarbonyl, with the expectation that some effect of the carbonyl on the reaction may appear.

Experimental Procedure

In the presence of dicobalt octacarbonyl or iron pentacarbonyl, the reaction between a gaseous mixture of carbon monoxide and hydrogen and a quantity of methylacrylate was conducted in an autoclave (1 l. in volume) of shaking type, at a constant pressure at a fixed temperature. The carbonyls were used for the reaction after they were dissolved in benzene. The rate of the reaction was estimated by the pressure decrease in a high pressure gas storage (1.6 l. capacity) from which the gas was continuously introduced into the autoclave in order that during the reaction the initial pressure in the autoclave might be maintained at the reaction temperature.

Since the use ratio of carbon monoxide to hydrogen in the reaction of hydroformylation was 1:1, the continuous supply of gaseous mixture comprising equal volumes of carbon monoxide and hydrogen into the autoclave causes scarcely any change of gas composition compared with the orginal gas composition in the autoclave. In this way a constant ratio of carbon monoxide to hydrogen of the gaseous mixture in the autoclave was kept throughout the reaction.

As for the reaction with dicobalt octacarbonyl, a reaction temperature of 110°C was preferred, at which the reaction proceeded with a measurable rate. At temperatures (100–104°C), a little lower than 110°C, the slow absorption of gas had already begun to take place. During this period of slow absorption, the gas was supplied from the gas storage into the autoclave up to the pressure which would be expected by steadily increasing temperature up to 110°C if there no absorption. The temperature rise from 100 to 110°C usually required about eight minutes. Once the temperature arrived at 110°C, both the temperature and the pressure were kept constant during further progress of the reaction.

β-carbmethoxypropionaldehyde could not be obtained in a yield as expected theoretically from the amount of gases absorbed in the reaction, and the maximum yield atained to only 80% of the theoretical*.

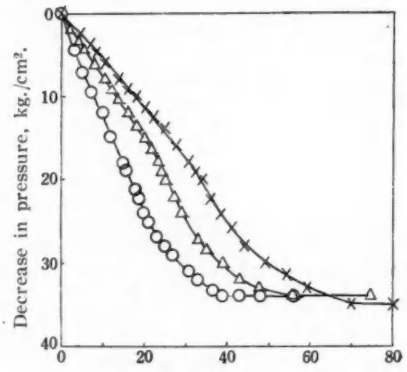
Dicobalt octacarbonyl was prepared according to the procedure by I. Wender et al.[5]: namely a slurry of 30 g. cobalt (II) carbonate in 200 cc. of petroleum-ether was treated with water-gas under a pressure of 200 kg./cm² in 1 l autoclave at 150°C for two hours, and the petroleum-ether solution of the carbonyl was cooled in dry ice for a short period of time, whereupon the crystalline dicobalt octacarbonyl separated. The crystallite was stored under the high pressure of carbon monoxide in a steel vessel, and a quantity of it was dissolved in 100 cc. of benzene immediately before use. Methylacrylate was supplied by the Toa Gosei Company and was 98% in purity. It was used without any further purification.

The reaction with iron pentacarbonyl was first conducted under conditions identical with those for dicobalt octacarbonyl, but it appeared soon that another kind of reaction took place, as will be described later. Iron pentacarbonyl was manufactured as was reported by one of the authors of this paper et al.[6] previously.

Results

Hydroformylation of Methylacrylate in Presence of Dicobalt Octacarbonyl.—The reaction was first carried out at a fixed partial pressure of hydrogen with different partial pressures of carbon monoxide, and then at a fixed partial pressure of the latter with different partial pressures of the former.

In Fig. 1 are shown the results obtained in a series of the experiments carried out at a constant pressure of hydrogen with different partial pressures of carbon monoxide, using 92 g. of methylacrylate and 1.72 g. of dicobalt octacarbonyl in 100 cc. of benzene. Three curves in the figure reveal the pressure decrease in the gas storage



Every experiment was conducted at 110°C under a constant hydrogen pressure (97 kg./cm².), with different carbon monoxide pressures of 21 (—○—), 52 (—△—), and 99 kg./cm². (—×—) respectively.

Fig. 1. Decrease in pressure of gas storage with time.

4) A. Asinger and O. Berg, *Ber.*, **88**, 445 (1955).

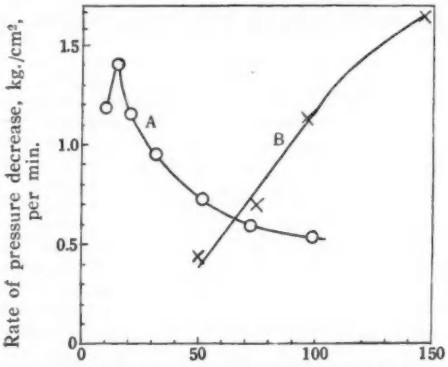
* The aldehyde was determined according to the procedure by H. Adkins et al.[1] Even though the distillation was made, after an addition of a small quantity of hydroquinone, at as low a pressure and as rapidly as was possible, it seemed difficult to isolate aldehyde without a considerable loss.

5) I. Wender, H. Greenfield and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2659 (1951).

6) H. Uchida and T. Minegishi, *Rpt. Govt. Chem. Ind. Res. Inst. Tokyo*, **45**, 1 (1950).

with time. A linear relation of the pressure decreae to time is observed during a time interval between the ten-minute and thirty-minute periods from the beginning of the reaction, and the slopes of the straight line give the rate of the reaction.

The dependence of the rate upon the partial pressure of carbon monoxide is given by curve A in Fig. 2. The rate attains the maximum value



A: hydrogen partial pressure, 97 kg./cm².
B: carbon monoxide partial pressure, 21 kg./cm².

Fig. 2. Relation of rate of hydroformylation to partial pressure of carbon monoxide (A) or hydrogen (B).

at a carbon monoxide pressure of 15 kg./cm². At a lower carbon monoxide pressure of 11 kg./cm² the absorption of the gas remained incomplete, proceeding to only half the theoretically available extent and part of the carbonyl was found to decompose into precipitates of a composition which is unclarified as yet. At the carbon monoxide pressure higher than 15 kg./cm² the hydroformylation** proceeded to completion because of the absorption of the theoretical amount of the gas, but the absorption took place rather slowly. In this case any decomposition of the carbonyl was hardly recognized after the reaction.

Curve B in Fig. 2 reveals the rate as a function of the hydrogen partial pressure at a fixed partial pressure of carbon monoxide. At hydrogen pressures higher than 75 kg./cm², the gas was absorbed in an amount just necessary for the hydroformylation of methylacrylate; however, at the lower pressures it was absorbed in only half the theoretical amount. In the former case the carbonyl persisted unchanged during the reaction, whereas in the latter case part of the carbonyl underwent decomposition. The high pressure of hydrogen has thus proved to be a requisite for the carbonyl to remain undecomposed in the reaction.

** Hydrogenation of β-carbmethoxypropionaldehyde as well as of methylacrylate seemed not to take place, as hydrogen was absorbed in an amount equal in mole to that of carbon monoxide.

The tendencies presented here agree with the results obtained by G. Natta on the hydroformylation of cyclohexene.

A. R. Martin[7] proposed a rate equation for the case of hydroformylation of di-isobutene,

$$\text{initial rate} = a p_{H_2}/(b p_{H_2} + c p_{CO}) \cdot [CO_2(CO)_8][C_8H_{15}]$$

where a, b, and c are constants. According to the equation the initial rate tends to decrease always with the rising carbon monoxide pressure. The tendency is in agreement with the present results obtained in a range of high carbon monoxide pressures, but is not so with those in a range of low pressures. In the latter case the carbonyl has been found to decompose during the reaction, and this is probably the reason why the rate begins to diminish again in this range. As for the dependence of the rate upon hydrogen pressure the equation suggests that, when b is not much greater than c, the rate tends to increase rather proportionally with the hydrogen pressure and then more slowly with the further increasing pressure. This is also consistent with the present results.

Hydrogenation of Methylacrylate in Presence of Iron Pentacarbonyl.—In the presence of iron pentacarbonyl, no reaction between methylacrylate and a gaseous mixture composed of carbon monoxide and hydrogen proceeded at 110°C, but at the higher temperature of 160°C the absorption of gas was found to take place if carbon monoxide partial pressure remained considerably low. Of the two gaseous reactants only hydrogen was absorbed to such an extent that, at the maximum absorption, the absorbed hydrogen amounted to one mole for one mole of methylacrylate, whereas the carbon monoxide was absorbed in extremely small amounts (0.03–0.04 mol.).

No absorption of hydrogen was observed in the reactions, either in the presence or absence of carbon monoxide conducted with iron catalysts such as the reduced one from iron oxide and the other one produced by thermal decomposition of iron pentacarbonyl.

The product of the reaction was confirmed as methylpropionate***.

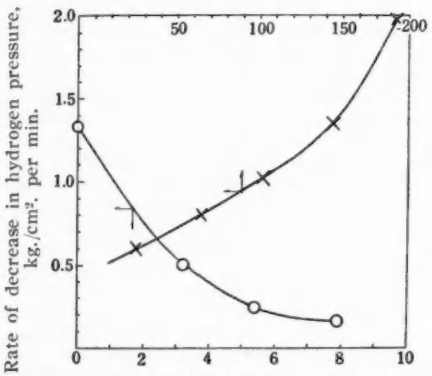
In order to see the effect of the partial pressure of an individual gaseous component on the reaction rate, the reaction was conducted at a fixed hydrogen pressure with varying carbon monoxide pressures and with varying hydrogen

7) A. R. Martin, *Chem. and Ind.*, **1536** (1954).

*** The confirmation was made as follows. Since the boiling temperatures of methylpropionate and benzene differed too little to permit the separation from each other by distillation, the synthesis of the product for the confirmation was carried out without any addition of benzene. In this case the hydrogen absorption proceeded to only three quaters of the theoretical extent. About 70% of the product distilled out at 78—80°C, leaving a higher boiling residue of polymerized products of methylacrylate. After the distillate had been freed from iron pentacarbonyl by adding mercuric chloride together with aceton and water, 70% of the distillate distilled out again at 79—79.5°C which corresponded to the b.p. of methylpropionate. The second distillate has a saponification value of 630. It contains a minute quantity (1%) of methylacrylate as determined according to the procedure by D.W. Beesing et al. using dodecanethiol (*Anal. Chem.*, **21**, 1073 (1949)).

pressures without an addition of carbon monoxide. During the reaction only hydrogen, but not a mixture of carban monoxide and hydrogen, was introduced into the autoclave from the gas storage. After the reaction without carbon monoxide the gaseous product contained about one per cent of carbon monoxide.

The initial rate obtainable from the initial tangent drawn to the curves for the pressure in the gas storage during the reaction vs. time is given in Fig. 3 as functions of carbon monoxide and hydrogen pressures respectively****. The reduction of methylacrylate by hydrogen takes place even in the presence of carbon monoxide at a pressure of 8 kg./cm². The lower the carbon monoxide pressure is, the higher the rate is; and the higher the hydrogen pressure is, the more rapidly the reaction proceeds.



Raw meterials: 92 methylacrylate and 10 g. iron pentacarbonyl in 100 cc. of benzene.

—○—: under a hydrogen partial pressure of 155 kg./cm².

—×—: in the absence of carbon monoxide.

Fig. 3. Relation of rate of hydrogenation to partial pressure of carbon monoxide or hydrogen pressure.

**** In this series of experiments the absorption of gas at the temperature lower than 160°C was small and hence the initial tangent served for the representation of the initial rate.

M. Orchin[8] stated that although ethylacrylate could be hydroformylated in the presence of dicobalt octacarbonyl it could not be reduced. The present results show that methylacrylate can be reduced in the presence of iron pentacarbonyl.

Summary

Hydroformylation of methylacrylate in the presence of dicobalt octacarbonyl was investigated by paying a special attention to the effect of varying ratios of carbon monoxide to hydrogen on the rate. The rate attains the maximum value at a certain partial pressure of carbon monoxide, and increases with the increasing partial pressure of hydrogen. The tendencies agree with the results obtained by G. Natta on the hydroformylation of cyclohexene. The rate equation proposed by A. R. Martin with respect to the rate of hydroformylation of di-isobutene can represent the tendencies observed in the present results.

In the presence of iron pentacarbonyl, methylacrylate has been found to be reduced to methylpropionate under high pressure of hydrogen containing carbon monoxide. The reduction becomes more difficult with the increasing partial pressure of carbon monoxide, but was made catalytically neither by an iron catalyst reduced from iron oxide nor by the one produced by the thermal decomposition of iron pentacarbonyl.

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8) M. Orchin, *Advances in Catalysis*, **5**, 391 (1953).

Tie Line Correlation for Ternary Liquid Equilibria

By Kiyoharu ISHIDA

(Received April 9, 1956)

Since only a few tie lines have been experimentally determined in most systems described in the literature, several methods of interpolating and extrapolating such data over the entire range of composition have been devised. Except for the graphical methods[1,2], they are expected to give a straight line from the appropriate plot of conjugate values at equilibrium. Most of these are related to the systems which comprise two miscible pairs of liquids and one partially miscible pair (type 1), while only a few methods[3,4,5]

1) "International Critical Tables", McGraw-Hill Book Company, Inc., New York (1928), Vol. III, p. 398. T.K. Sherwood, "Absorption and Extraction", McGraw-Hill Book Company, Inc., New York (1937), p. 242. A. V. Brancker, T. G. Hunter and A. W. Nash, *Ind. Eng. Chem., Anal. Ed.*, **12**, 35 (1940).

2) D. B. Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

3) K. A. Varteressian and M. R. Fenske, *Ind. Eng. Chem.*, **29**, 270 (1937).

4) T. F. Brown, ibid., **40**, 103 (1948).

5) J. B. Conway and J. B. Philip, ibid., **45**, 1083 (1953).

have been proposed to the systems which comprise two partially miscible pairs of liquids and one miscible pair (type 2).

It seems that no useful method applicable to both types has ever been proposed, thus, the method useful for type 1 does not always give satisfactory results when applied to type 2 and vice versa[6,7]. Since it is evident that both types may interchange with each other with changing temperatures, the useful method applicable for both types is desirable, if it is possible.

The upper critical solution temperature in the binary system containing toluene and liquid ammonia was found to be −7.4°C by the measurement of mutual solubilities of this system. Therefore, the equilibrium for the system *n*-heptane-toluene-liquid ammonia at the temperatures below −7.5°C involves two pairs of partially miscible liquids, and the binodal curve of the system at −7.5°C touches the side of the triangle which represents the binary mixture of toluene and liquid ammonia. It is considered that the methods resulting in a straight line for the tie-line data at the critical solution temperature of one pair of binary systems are generally applicable to systems for both types.

In the present study, the system *n*-heptane-toluene-liquid ammonia has been investigated at −7.5° and −15°C to determine whether the previous methods for obtaining the straight line correlation were applicable to both types independent of temperature.

Experimental Procedure and Results

The equilibrium data for the ternary system and mutual solubilities of toluene and liquid ammonia at the temperatures of −10°, −15° and −20°C were determined by the same way as described in the previous paper[8]. Alcohol cooled by dry ice in the Dewar vessel of large capacity was used as a constant temperature bath, and the desired temperature could be maintained within the range of ±0.1°C throughout the experiment. In order to minimize the change of temperature, thermal insulating tubes were used by means of which alcohol was made to circulate around the bottle containing the system. The heterogeneous liquid layers were separated and analysed after the saturation equilibrium was attained. The mutual solubilities of toluene and liquid ammonia at temperatures near the critical solution temperature were determined by noting the miscibility temperatures of mixtures of known composition. In these cases, the vapor pressure of a saturated solution at that temperature was determined experimentally, and the necessary correction for the composition of liquid components was estimated using the vapor pressure data and the volume of the vapor space.

The experimental data for the binary system toluene-liquid ammonia are given in Table I and the equilibrium data for the ternary system are given in Table II and shown in Fig. 1 and 2. In

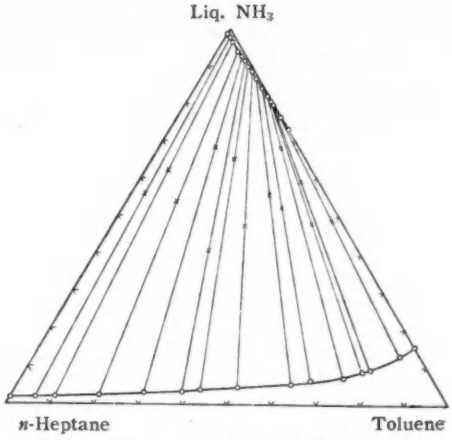

Fig. 1. System *n*-Heptane-Toluene-Liq. NH_3 at −15°C, wt. %.

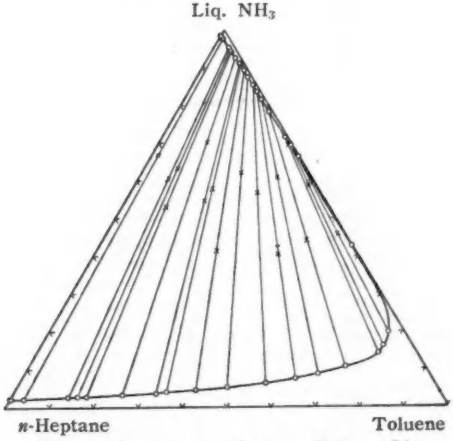

Fig. 2. System *n*-Heptane-Toluene-Liq. NH_3 at −7.5°C, wt. %.

TABLE I

SOLUBILITY DATA FOR THE SYSTEM TOLUENE AND LIQ. NH_3

Temperature °C	Wt. % NH_3 in NH_3 rich Layer	Wt. % NH_3 in Toluene rich Layer
−10	64.4	20.2
−15	73.2	15.3
−20	78.6	12.4

Cloud Point, °C	Wt. % NH_3 in Solution
−8.0	29.3
−7.6	35.9
−7.4	39.6
−7.4	41.1
−7.5	46.0
−7.8	54.4
−7.8	56.1
−8.3	59.7

6) C. E. Dryden, ibid., 35, 492 (1943).
7) D. DeB. Darwent and C. A. Winkler, *J. Phys. Chem.*, 47, 442 (1943).
8) K. Ishida, *J. Chem. Soc. Japan* (Ind. Chem. Sect.,) 56, 469 (1953).

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEPTANE-TOLUENE-LIQUID AMMONIA

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Toluene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Toluene Wt. % in the Raff. (Solvent-free Basis)	NH_3 Wt. %	Toluene Wt. % in the Ext. (Solvent-free Basis)
		At −15.0°C			
0.0	—	1.7	0.0	98.8	0.0
6.8	56.0	1.8	5.7	97.7	43.5[a]
13.3	62.4	2.0	10.3	96.4	59.5[a]
24.2	53.8	2.4	20.3	93.9	75.0
39.8	68.4	3.1	30.7	92.7	85.0
42.6	41.2	3.4	39.5	91.6	88.8
52.9	65.3	4.0	43.6	89.9	89.9
56.9	47.5	4.6	52.7	88.6	93.0
70.5	55.7	5.4	65.2	86.7	95.1
75.0	52.5	6.5	70.0	84.2	96.1
86.1	68.2	7.1	78.2	82.0	97.7
86.1	48.1	8.8	83.4	80.6	98.3
90.0	59.5	9.3	85.4	79.7	98.3
96.0	49.1	12.9	94.8	76.6	99.0
100.0	—	15.3	100.0	73.2	100.0
		At −7.5°C			
0.0	—	2.2	0.0	98.5	0.0
4.0	67.0	2.2	2.9	97.7	25.4[a]
17.7	60.6	2.7	13.3	95.3	72.1[a]
21.0	63.5	2.8	15.3	94.7	74.6[a]
21.5	53.0	2.8	17.5	94.3	77.0[a]
36.5	70.3	3.3	25.7	92.6	83.8[a]
39.7	54.9	3.7	33.4	90.9	87.7[a]
43.2	58.0	4.1	35.8	90.6	89.0
46.8	41.4	4.6	42.6	89.2	91.0
59.6	62.2	5.3	50.1	87.6	92.6
66.8	56.9	6.4	59.3	85.5	94.1
69.7	40.5	7.5	66.6	83.7	95.3
80.0	61.0	8.8	72.6	81.5	96.0
82.7	44.1	10.5	79.9	78.4	97.0
96.6	69.5	14.1	90.0	71.5	97.9
95.7	58.9	16.0	92.3	69.2	98.4
96.6	45.8	19.7	95.6	66.1	99.0
100.0	—	42.5[b]	100.0	42.5[b]	100.0
		At 0.0°C			
0.0	—	2.7	0.0	98.2	0.0
15.4	68.3	3.4	9.8	95.5	76.0
15.4	47.8	3.6	12.2	94.8	79.0
19.5	44.3	3.7	16.3	93.9	83.0
37.9	68.9	4.1	25.3	91.3	87.5
37.9	54.4	4.7	30.2	90.2	88.5
47.4	61.3	5.0	36.7	88.3	89.8
53.7	61.2	5.6	42.1	86.0	90.1
47.4	34.2	5.9	43.4	84.9	90.5
53.7	36.3	6.7	49.8	83.8	91.3
74.0	61.8	8.2	60.4	79.9	92.9
74.0	39.9	10.8	70.3	76.3	93.7
84.3	61.0	12.2	75.2	74.2	94.7
84.3	31.2	15.8	82.8	66.7	95.2

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Toluene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Toluene Wt. % in the Raff. (Solvent-free Basis)	NH_3 Wt. %	Toluene Wt. % in the Ext. (Solvent-free Basis)
91.0	48.2	20.9	87.9	62.3	95.4
91.0	35.4	23.9	90.2	58.2	95.6
93.7	45.1	29.5	92.2	52.6	95.4
Plait Point[c]		45.4	94.8	45.4	94.8
		At 20.0°C			
0.0	—	4.8	0.0	96.9	0.0
8.7	48.3	5.4	6.6	93.8	41.1
19.5	40.1	6.6	16.4	89.7	61.7
28.4	67.1	6.6	17.3	89.3	62.5
29.5	50.3	7.4	22.8	86.4	69.1
29.5	44.0	7.5	24.2	86.0	71.2
37.9	62.1	7.7	25.4	85.6	71.9
49.1	64.0	9.0	32.3	81.6	75.6
37.9	35.1	9.1	33.6	81.5	76.3
49.1	35.0	11.8	44.4	75.8	79.4
59.4	49.3	13.4	49.3	72.3	80.3
59.4	39.2	15.3	53.6	69.4	81.0
70.7	56.3	16.8	56.7	67.2	80.6
70.7	43.4	22.7	64.5	57.8	78.9
74.1	43.3	30.8	69.6	47.5	76.4
Plait Point[c]		43.4	75.0	43.4	75.0

a) This value was calculated from the concentrations of ammonia in both layers and the compositions of the total mixture and raffinate.
b) The upper critical solution temperature for the binary mixtures of toluene and liquid ammonia is −7.4°C. But, since in the equilibrium temperature the change of temperature within ±0.1°C was inevitable, the composition at the critical point were estimated to be the same as the solubility of toluene at −7.5°C.
c) The plait point was estimated according to Treybal et al.[9]

addition to the data at −15° and −7.5°C, the equilibrium data at the temperatures of 0° and 20°C for this ternary system are also given in Table II for convenience of discussion, as these data have not been presented in the previous paper[8]. It is found that in the neighborhood of the critical solution temperature for the binary mixtures of toluene and liquid ammonia, the selectivity[10] of liquid ammonia for toluene which is defined by the difference between the concentration of the solute in the extract, free from the solvent, and the corresponding concentration in the raffinate, is almost unaffected with the change of temperature at the higher concentrations of toluene, but at the lower concentrations of toluene its selectivity increases as the temperature rises to about 0°C. The effect of temperature on the selectivity will be discussed in the later paper.

Discussion

It has already been found that the Hand plot[2] and the Othmer-Tobias plot[11] give a straight line for the data at 20° and 0°C[8], but these plots were unsatisfactory for the data at −7.5° and −15°C, showing the curvature at the higher concentrations of toluene. This can be shown more conveniently by using a notation where E is the solute distributed between the substantially immiscible diluent R and solvent S, and the suffix r and s represent the concentration in the raffinate and the extract layer, respectively. It is clear that good results cannot be obtained for the systems of type 2 by these methods, because the values on the one hand give the definite values in all concentrations of the solute, while, the values on the other hand become infinite at $R=0$ on these coordinates, where a plot of conjugate values of Es/Ss against Er/Rr or $(1-Ss)/Ss$ against $(1-Rr)/Rr$ is made on double logarithmic coordinates.

Brown plot[4] of conjugate values of Rr/Ss against Rr made on arithmetic coordinates, which has been found to be applicable for the systems of type 2, gave lines of considerable curvature for the present data. Both methods of Conway and Philip[5] plotting the conjugate values of log Ss against Rr and Varteressian and Fenske[3] in which the equa-

9) R. E. Treybal, L. D. Weber and J. F. Daley, *Ind. Eng. Chem.*, 38, 817 (1946).
10) K. Ishida, *Sience Repts. Research Inst. Tohoku Univ.*, Ser. A, 5, 377 (1953); *C. A.*, 48, 9045h (1954).
11) D. F. Othmer and P. E. Tobias, ibid., 34, 693 (1942).

tion of distribution ratio may be represented by hyperbola and a straight line results from a plot of Es/Er against Es in the systems of type 2, did not give good results showing large curvature at higher concentrations of toluene.

No satisfactory method giving a straight line by the simple plot for the present data was found in many other previous methods in which a plot of conjugate values of Ss/Rr against Ss proposing by Bachman[12], Smith plot[13] of conjugate values of log (Es/Er) against log Es, Campbell plot[14] of log Es against log Er at equilibrium, and a plot of log $(1-Es)/Es$ against log $(1-Er)/Er$ by Major and Swenson[15] were included.

Of these methods just described, coordinates by Othmer and Tobias and Conway and Philip indicated a relatively good straight line except for the higher concentration of toluene.

The method by Dryden[5] which correlates the concentrations of the solute at equilibrium phases on the solvent free basis, namely a plot of conjugate values of $\{Er/(Er+Rr)\}/\{Es/(Es+Rs)\}$ against $Er/(Er+Rr)$, showed goood results for the data at the temperatures of $-15°$, $-7.5°$ and 0°C, but was unsatisfactroy for the data at 20°C, since the relative distribution ratio was not always constant, as he pointed out.

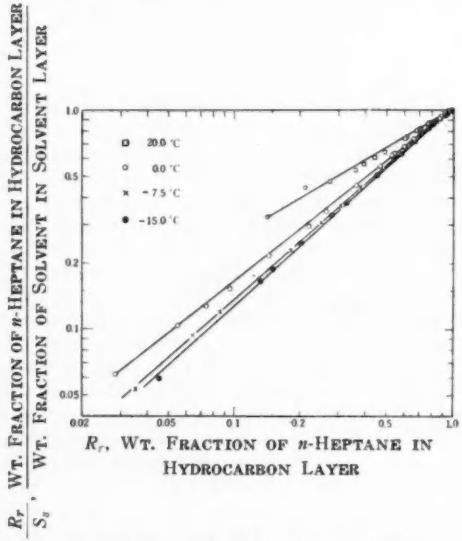

Fig. 3. Plot on logarithmic coordinates of R_r/S_s against R_r for the system *n*-Heptane-Toluene-Liq. NH_3.

12) I. Bachman, ibid., Anal. Ed. **12**, 38 (1940).
13) A. S. Smith. ibid., **42**, 1206 (1950).
14) J. A. Campbell, ibid., **36**, 1158 (1944).
15) C. J. Major and O. J. Swenson, ibid., **38**, 834 (1946).

Tests of these methods for the system *n*-hexane-methylcyclopentane-aniline[7], which is another system investigated at several temperatures neighbouring the critical solution temperature for the binary mixtures of the solute and the solvent, indicated the same results as the present data.

The author has found that a straight line results from a plot of log (Rr/Ss) against log Rr at equilibrium, where Ss is the fraction of the solvent in the solvent phase and Rr is the fraction of the diluent in the diluent phase. Plots by this method for the present data at the various temperatures are shown in Fig. 3, and for the system of *n*-hexane-methylcyclopentane-aniline[7] in Fig. 4. In Fig. 4, plots for the systems using liquid ammonia as a solvent are also included. It is clear that satisfactory results are obtained not only for the systems of type 2, but also type 1. In Fig. 5, several systems investigated by various

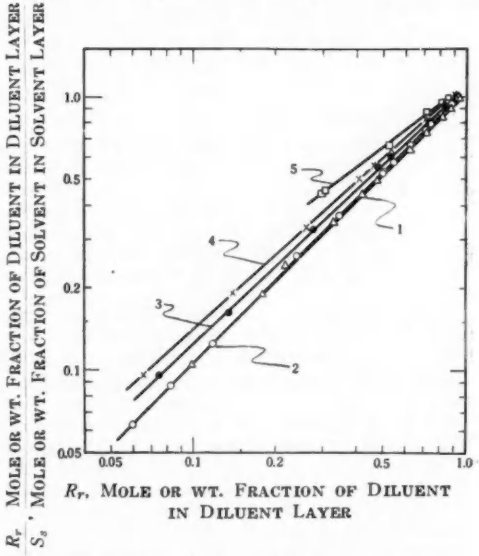

Fig. 4. Plot on logarithmic coordinates R_r/S_s against R_r for the systems *n*-Hexane-Methylcyclopentane-Aniline (3, 4, 5), *n*-Hexane-Cyclohexane-Liq. NH_3 (2) and *n*-Heptane-Octene-1-Liq. NH_3 (1).

Number	System R	System E	System S	Temperature, °C	Reference
1	*n*-Heptane-Octene-1-Liq.	NH_3, wt. fraction.		20.0	(16)
2	*n*-Hexane-Cyclohexane-Liq.	NH_3, wt. fraction.		20.0	(16)
3	*n*-Hexane-Methylcyclopentane-Aniline,	mole fraction.		25.0	(7)
4	*n*-Hexane-Methylcyclopentane-Aniline,	mole fraction.		34.5	(7)
5	*n*-Hexane-Methylcyclopentane-Aniline,	mole fraction.		45.0	(7)

16) K. Ishida, *J. Chem. Soc. Japan*, (Ind. Chem. Sect.), **57**, 479 (1954).

workers are plotted and plots for systems having the distribution ratio greater than unity are shown in Fig. 6. These systems were selected at random. Among the systems represented by two straight lines changing their slopes, the system water-isopropanol-benzene and the system *n*-heptane-pyridine-liquid ammonia are the instances, in which curves or two straight lines having different slopes have also been obtained by the other methods.

Although plots for all systems do not always give a straight line, the plotted data fall on straight lines almost within their probable experimental accuracy, and especially for the systems containing two pairs of partially miscible liquids fair straight lines are obtained.

The straight lines can be represented by equations of the form

$$\log (Rr/Ss)=n \log Rr+m \quad (1)$$

If the value of n is near unity, letting $m=\log m'$, it follows approximately,

$$Rr/Ss=m'Rr \quad (2)$$

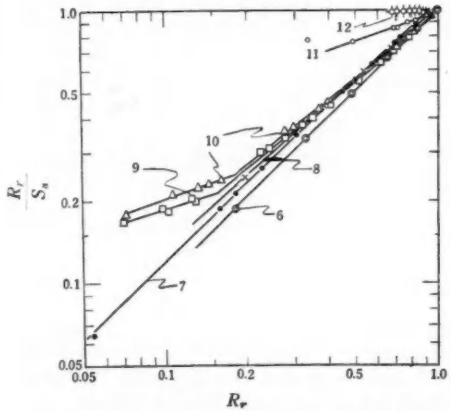

Fig. 5. Plot on logarithmic coordinates of R_r/S_s against R_r for systems of various investigators.

Number	System R	E	S	Temperature, °C	Reference
6	Toluene-	Aniline-	Water	25	(17)
7	*n*-Heptane-	Methylcyclohexane-	Aniline	25.0	(3)
8	1,1,2-Trichloroethane-	Methyl ethyl Ketone-	Water	25	(18)
9	Water-	Acetic acid-	Toluene	25	(19)
10	Water-	Acetic acid-	Benzene	25	(2)
11	Water-	Acetaldehyde-	Toluene	17	(20)
12	Water-	Acetic acid-	Furfural	26.7	(21)

17) J. C. Smith and R. E. Drexel, *Ind. Eng. Chem.*, **37**, 601 (1945).
18) M. Newman, C. B. Hayworth and R. E. Treybal, ibid., **41**, 2039 (1949).
19) R. M. Woodman, *J. Phys. Chem.*, **30**, 1283 (1926).
20) D. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **34**, 690 (1942).
21) A. E. Skrzec and N. F. Murphy, ibid., **46**, 2245 (1954).

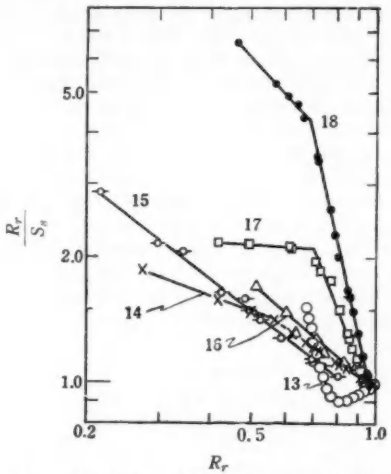

Fig. 6. Plot on logarithmic coordinate of R_r/S_s against R_r for systems having distribution ratio more than unity. (except for No. 16)

Number	System R	E	S	Temperature, °C	Reference
13	Water-	Isopropanol-	Benzene	25.0	(22)
14	Water-	Acetone-	1,1,2-Trichloroethane	25.0	(10)
15	Water-	Dioxane-	Benzene	25.0	(23)
16	Water-	Methanol-	Butanol	0.0	(24)
17	*n*-Heptane-	Pyridine-	Liq. NH_3	20.0	(25)
18	*n*-Heptane-	Pyridine-	Liq. NH_3	0.0	(25)

The method represented by equation 2 is that of Brown[4], of course. Therefore, it is possible to say that the author's method is Brown's generalized. In this plot, it is clear from equation 1 that a straight line will be obtained by using mole fraction on values of Rr and Ss, as well as weight fraction.

In equation 1, m is estimated from the mutual solubilities of R and S. When the same components are used for the diluent and the solvent, there is another possibility that the distribution ratio of the various solutes distributed between the diluent and the solvent can be compared by the values of slope n at the same temperature, since the value of m becomes constant, and distribution curves of the various solutes are given by lines which have various slopes and converge to a point representing the value of m.

If the value of n does not equal unity in equation 1 in all cases, equation 3 can be followed.

$$\log (Ss/Rr)=\{n/(n-1)\} \log Ss+m/(n-1) \quad (3)$$

22) A. L. Olsen and E. R. Washburn, *J. Am. Chem. Soc.*, **57**, 303 (1935).
23) R. J. Berndt and C. C. Lynch, ibid., **66**, 282 (1944).
24) A. J. Mueller, L. I. Pugsley and J. B. Ferguson, *J. Phys. Chem.*, **35**, 1314 (1931).
25) K. Ishida, *Bull. Chem. Res. Inst. Non-Aqueous Sol.*, Tohoku Univ., **3**, 109 (1953).

Therefore, it is possible to consider that the author's method is the modification of the Bachman plot, and a plot using equation 3 is also possible. However, the application of equation 3 for the systems containing the formation of two pairs of partially miscible liquids gives lines of curvature which approach the definite values at the infinite, since the value of n in these systems almost equals unity.

It is interesting that the method of Othmer and Tobias and the method presented in this paper are introduced by modifying the method of Bachman.

Summary

The various methods for obtaining straight lines were examined for the tie-line data investigated at several temperatures near the critical solution temperature for binary mixtures of the solute and the solvent, and the following results were obtained.

1. The Hand plot and the Othmer and Tobias plot which are useful for the systems containing one partially miscible pair are unsatisfactory for the systems containing two partially miscible pairs.

2. The method proposed by Brown and the method by Conway and Philip which have been said to be applicable for the systems containing the formation of two pairs of partially miscible liquids do not give good results for the systems at temperatures near the critical solution temperature for binary mixtures of the solute and the solvent.

3. If a plot is made of the logarithm of the ratio of the concentration of the diluent in the diluent phase to the concentration of the solvent in the solvent phase against the logarithm of the concentration of the diluent in the diluent phase, a straight line will be obtained not only for systems containing two partially miscible pairs, but also for systems containing one partially miscible pair.

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Non-Newtonian Viscosity of Dilute High Polymer Solutions. II. Measurements on Polystyrene Fractions in Toluene*

By Toshiaki KUROIWA

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Introduction

During recent years it has been recognized by several investigators that the non-Newtonian behavior of polymer solutions can no longer be ignored in the evaluation of the intrinsic viscosity (limiting viscosity number), $[\eta]$, in some cases. As the result, various investigators[1-8] have recently examined the shear-rate dependence of viscosity of dilute polymer solutions and some have proposed the methods of extrapolating the viscosity data to the limit of zero rate of shear.

Most of the empirical equations[9-12] that have been proposed to express the shear dependence of $[\eta]$ or reduced viscosity, η_{sp}/c, show the velocity gradient entering to the first power. For example, Fox, Fox and Flory[9] have proposed the empirical relationship:

$$\ln \eta_{sp} = [\ln \eta_{sp}]_0 - (\phi/100)q, \qquad (1)$$

where $[\ln \eta_{sp}]_0$ is the value of $\ln \eta_{sp}$ at zero rate of shear, ϕ is a constant which is independent of concentration in a given solvent, and q denotes the velocity gradient. These equations are in marked disagreement with the prediction of the theory of Kuhn and Kuhn[13] according to which $[\eta]$ should decrease

* Presented at the 9-th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1956.

1) P. Alexander and K. A. Stacey, *Trans. Faraday Soc.*, **51**, 299 (1955).
2) J. Schurz, *Makromol. Chem.*, **12**, 127 (1954).
3) M. A. Golub, *J. Polymer Sci.*, **18**, 27, 156 (1955).
4) F. Patat and J. Hartmann, *Makromol. Chem.*, **18/19**, 422 (1956).
5) T. Hotta, *Chem. High Polymers*, **12**, 276 (1955).
6) M. A. Golub, *J. Phys. Chem.*, **60**, 431 (1956).
7) T. Kuroiwa, This bulletin, **29**, 164 (1956).
8) See also the literatures cited in the previous paper (7) 1—16), 20) for this subject.
9) T. G. Fox, Jr., J. C. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1901 (1951).
10) H. T. Hall and R. M. Fuoss, ibid., **73**, 265 (1951).
11) G. de Wind and J. J. Hermans, *Rec. trav. Chim. Pay-Bas*, **70**, 521 (1951).
12) S. Newman, L. Loeb and C. M. Conrad, *J. Polymer Sci.*, **10**, 463 (1953).
13) W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533 (1945).

initially with q^2, and accordingly $[\eta]$ vs. q curve should have horizontal tangent at $q=0$.

Kuhn and Kuhn[13] have suggested that the non-Newtonian character of polymer solution depends on the ease with which the chain molecule is deformed. Thus for a fairly rigid molecule, since the orientation of the chain molecule in the direction of flow increases as the gradient field increases and since the frictional resistance of the chain decreases with increasing orientation, $[\eta]$ decreases with increasing q. For a completely flexible or soft molecule, on the other hand, which can change its shape in flow and become stretched in the gradient field, $[\eta]$ is independent on q because of the complete compensation of stretching and orientation effects.

The viscous resistance which must be overcome by a force, which tends to change the end-to-end distance of a molecule, consists not only of the usual resistance of the surrounding medium but also of an additional resistivity-the inner viscosity of Kuhn and Kuhn-which is inherent in the molecular chain.

The resistance force due to the inner viscosity, K_2, can be written as follows:

$$K_2=-B\mathrm{d}h/\mathrm{d}t, \tag{2}$$

where h is the end-to-end distance of the molecule, and B may be called "the coefficient of stiffness" of the chain.

These authors have deduced for the limiting case of $B\gg\lambda\eta_0 L$ the following expression[14]:

$$[\eta]_q/[\eta]_0=1-2\xi^2+\frac{473}{16}\xi^4-\cdots\cdots \tag{3}$$

where

$$\xi=q\bar{h}_0^2/16\,D_{\mathrm{rot}}, \tag{3'}$$

and L is the so-called hydrodynamic length, i.e., the fully extended legnth of the chain, η_0 is the solvent viscosity and λ a numerical factor which is approximately equal to $3\pi/16$, $[\eta]_q$ is the intrinsic viscosity at a shear rate q and $[\eta]_0$ is the one at $q=0$, D_{rot} represents the rotational diffusion constant of the chain in the solution and $\bar{h}_0^2$ is the mean square end-to-end distance of the chain at rest. Moreover, it has been shown that the approximate value of ξ for a given polymer can be evaluated according to the equation:

$$\xi=[\eta]_0M\cdot10^3\eta_0q/mRT \tag{4}$$

where M and m are the molecular weight (MW) of the polymer and the monomer, respectively.

14) Kuhn and Kuhn treated the problem only in the two-dimensional motion on the xy-plane. The three dimensional treatment will change the numerical factors but not affect the functional dependence.

Real polymer chains are neither quite stiff nor completely soft, and the dependence of $[\eta]$ on q should lie somewhere between these limiting cases. Furthermore, according to the theory[15], B decreases with MW as $1/M$ owing to the increase of the number of links where a rotation can take place. Hence the shear rate effect should become progressively less pronounced with increasing MW, and this means that $[\eta]_q/[\eta]_0$ vs. ξ curve for real polymer should approach to $[\eta]_q/[\eta]_0=1$ (for $B\ll\lambda\eta_0L$) with increasing MW and to the curve according to Eq. (3) with decreasing MW[16].

In order to determine whether the increase in viscosity persists up to the region of very low rates of shear in accordance with the proposed empirical relations such as Eq. (1) or it vanishes in a range of small q as has been demanded by the theory, most of the existing data are of little avail because they are concerned only with regions of rather high q. It is worthy of notice that a few recent works[1,7,17] in which the measurements have been extended down to very low q appear to show the quadratic dependence of viscocity on q and thus to support the above-mentioned theory[18].

In the present paper the results of measurements on the shear dependences of several polystyrene fractions in toluene are presented and the effect of non-Newtonian behavior on the evaluation of $[\eta]$ and Huggins' slope constant k' are discussed from these data and some remarks are made as to $[\eta]$-MW relationship and the effect of polydispersity of polymer on the shear dependence of viscosity. Finally, a comparison is made between the above-mentioned theory and the results of the present investigation on the basis of $[\eta]_q/[\eta]_0$ vs. ξ relation.

Experimental

The original polystyrene was prepared by polymerizing the pure monomer at 60°C. The procedures for purification of the monomer and for polymerization of the monomer were described in the previous paper[7].

15) W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **29**, 609 (1946).

16) Of course, in a simple $[\eta]_q/[\eta]_0$ vs. q plot, such a tendency cannot be expected and the variation of $[\eta]_q/[\eta]_0$ with q is larger, the larger the MW is, as has been pointed out several investigators.

17) E. Wada, *J. Sci. Res. Inst.*, **47**, 159 (1953); *J. Polymer Sci.*, **14**, 305 (1954).

18) On the other hand, non-vanishing increase of viscosity at very small q was found to be real for some polymers. From this fact, Schurz has considered that the shear dependence is mainly caused by molecular interactions (formation of temporary structure), and that the contributions of the single molecules only play a role of minor importance. See the literature 19) for the further details.

19) J. Schurz, *Makromol. Chem.*, **10**, 194 (1953).

The fractionation of the polymer was carried out by precipitating the polymer from a mixture: polystyrene-methylethylketone-n-butanol. Methylethylketone was slowly evaporated at constant temperature by suction until precipitation began. The mixture was then heated until the precipitate redissolved and was allowed to stand overnight, after which time a fraction reprecipitated to gel at the original temperature. A fraction separated from the mixture was then dissolved in benzene to make up about 1% solution and reprecipitated in a large excess of methanol. This precipitate was washed with methanol and dried by pumping in vacuum at about 70°C for six hours. 22 fractions were obtained in this way[20].

Molecular weight (MW) of the original polymer (UF) and the fractions used in this study were determined by light scattering measurements of toluene solutions of these samples[21] and are listed below together with the viscosity data obtained by an Ostwald viscometer.

fraction	$MW\times10^{-4}$	$[\eta]$ (100 cc./g.) in toluene at 30°C	k'
F- 4	410	5.49	0.39
F-10	308	4.53	0.37
F-16	194	3.27	0.34
F-20	100	2.07	0.38
UF	283	4.01	0.33

The apparatus used in this work consists of a manostat system, a manometer and a horizontal viscometer. These were already described in detail in the previous paper[7] together with the experimental procedure employed, and are not repeated here.

The maximum rate of shear at the wall of the capillary was calculated by the equation[22]:

$$q=4Q/\pi R^3 t\times(1-1/4t\times \mathrm{d}(Pt)/\mathrm{d}P), \qquad (5)$$

and the relative viscosity, η_r, which corresponds to the above value of q was evaluated by the equation[22]:

$$\eta_r=t/t_0\times(1-1/4t\times \mathrm{d}(Pt)/\mathrm{d}P)^{-1}, \qquad (6)$$

where R is the radius of the capillary, P is the driving pressure and t and t_0 are the efflux times for a given volume, Q, of the solution and the solvent, respectively.

Results and Discussion

Figs. 1 and 2 show the products of applied pressure and efflux time, Pt, for these fractions, measured at several concentrations at 25°C, plotted against P, where t is the efflux time for unit volume of flow (Pt is nearly proportional to η_r). On casual inspection, the more concentrated the solution, the larger the shear dependence of viscosity. An examination of these results, however, reveals that

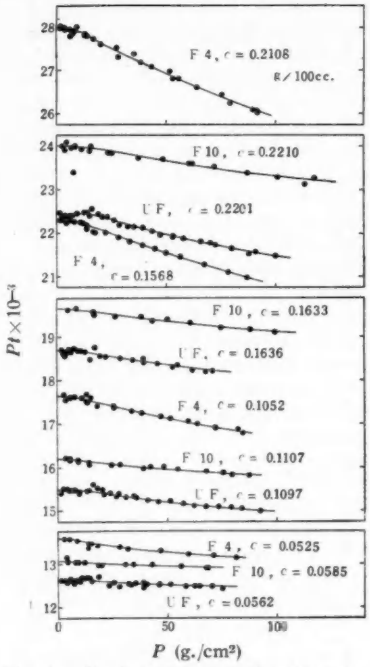

Fig. 1. Product of applied pressure and efflux time for unit volume of flow, Pt vs. applied pressure, P for F 4, F 10 and UF, measured at several concentrations at 25°C by a horizontal viscometer No. 1 (R=0.01440 cm, L=30.3 cm).

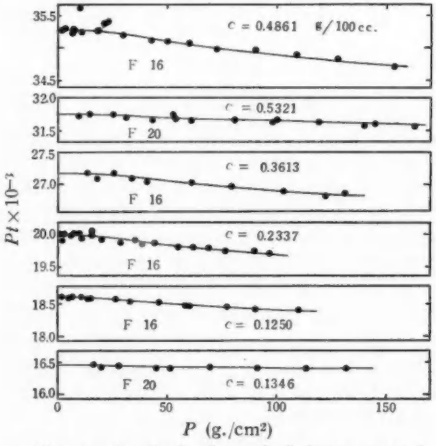

Fig. 2. Product of applied pressure and efflux time for unit volume of flow, Pt vs. applied pressure, P for F 16 and F 20 measured at 25°C. Results for F 16, c=0.1250 and F 20 were obtained by a horizontal viscometer No. 2 (R=0.01362 cm, L=30.1 cm) and the other by a horizontal viscometer No. 1.

20) Details of these procedures were described already in the *Annual Reports of Fiber Science Research Institute* (*Osaka University*), No. 9, p. 30 (1956), by K. Kawahara of this laboratory.

21) This author is indebted to T. Oyama and K. Kawahara of this laboratory for these measurements. Details of these will be published in near future.

22) T. Hotta, *Reports of Laboratory of High Polymer Research, Nagoya University*, No. 3, 22 (1951).

MW of the polymer has the most pronounced effect on degree of shear dependence; for example, the shear effect is quite small in the case of F 20 even when concentration is as high as 0.53%, but it is fairly large for F 4 even when concentration is ten times smaller than that of the solution of F 20.

It may be seem from these figures that these curves have horizontal tangents at the origin instead of showing sharp rises in the neighborhood of zero pressure, although this is somewhat ambiguous for the fractions of low *MW* owing to the rather large scattering of points in this region. Breadth of initial horizontal part seems to be roughly independent on concentration for a given fraction and it extends toward a high pressure as *MW* of fraction decreases. The tendency for solution viscosity to be constant at low pressures may be found also in Fig. 3, which

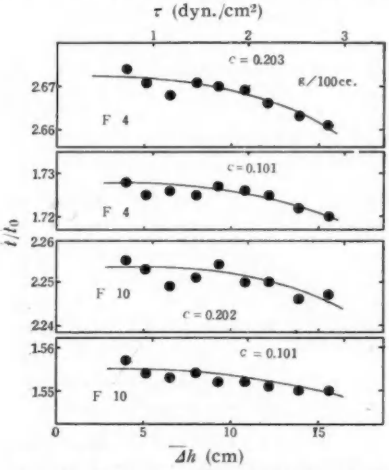

Fig. 3. Ratio of efflux times of solution and solvent, t/t_0, measured at 35°C by a multi-bulb viscometer (see foot-note (23)). $\bar{\Delta h}$ denotes the mean pressure head of the viscometer. For the upper abscissa, τ, see Eq. (7).

shows ratios of efflux times of solution and solvent measured by a specially designed multi-bulb viscometer[23] which is essentially similar to that designed by Schurz[2] as a function of the mean pressure head of the viscometer.

Included in Fig. 1 are the results obtained previously for UF, of which a description was already given in the earlier paper[7]. It is interesting to note that these solutions of UF exhibits the more pronounced shear dependences than the solutions of F 10 despite the fact that the average *MW* of F 10 is somewhat higher than that of UF and the concentration range covered by these two are approximately equal to each other. The characteristic feature of *Pt* vs. *P* relation also seems to be somewhat different between these two. This can be presumably ascribed to the presence of high *MW* components in UF. In this connection, it is very attractive to compare the shear dependences of viscosities of several solutions at the same concentration, the solute polymers of which are comparable to each other in average *MW* but different in patterns of *MW* distribution.

The results of measurements on two kinds of mixtures of two fractions and on single fractions are illustrated in Fig. 4, as *Pt* vs. *P* plots and these samples measured are tabulated in Table I. From these results, it

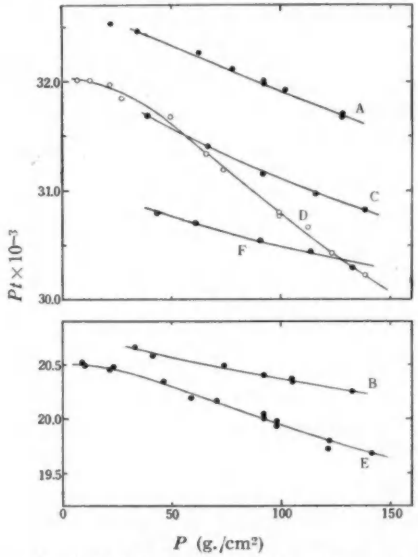

Fig. 4. Product of applied pressure and efflux time for unit volume of flow, *Pt* vs. applied pressure, *P* for the solutions shown in Table I, measured at 30°C by the viscometer No. 2 (see foot-note of Fig. 2). For A, B, C etc., see the last column of Table I.

seems that the shear effect should be considered dependent on patterns of *MW* distribution and is markedly affected by the presence of high *MW* components in the polymer mixture. This means that it might be possible to find somewhat smaller shear dependences of polystyrens fractions than those found in the present investigation if better fractionated samples were used, and so too quantitatively distinct interpretation of the present

23) The design of the viscometer (R=0.0131 cm, L=30 cm) and results for the other solutions obtained by the viscometer will be published in this bulletin in near future.

TABLE I

SAMPLES USED IN THE MEASUREMENTS RESULTS OF WHICH ARE SHOWN IN FIG. 3

Sample	Component, Weight%	$[\eta]^a$	Concentration in g./100 cc.	
F- 12	——	3.98	0.3022	A
			0.1510	B
MF-1	F 8 ($[\eta]^a$=4.91), 36.2	3.86[b]	0.3022	C
	F 16 ($[\eta]^a$=3.27), 63.8	(calc'd)		
MF-2	F 4 ($[\eta]^a$=5.49), 52.2	3.85[b]	0.3022	D
	F 20 ($[\eta]^a$=2.07), 47.8	(calc'd)	0.1512	E
F- 13	——	3.76	0.3022	F

a measured by an Ostwald viscometer in toluene at 30°C.
b calculated from $[\eta]$ of each component assuming contribution of components to the viscosity of mixture by their weight fractions.

results must be abandoned.

For each of these solutions, η_r was calculated as a function of q by the use of Eqs. (5) and (6) from the results in Figs. 1 and 2, and from the data for the dimensions of the viscometer. A typical set of η_r vs. q curves for F 4 is shown in Fig. 5. Values of η_{sp}/c were interpolated from these η_r vs. q relations at various q and plotted against the concentration for F 4 and F 10 as shown in Fig. 6.

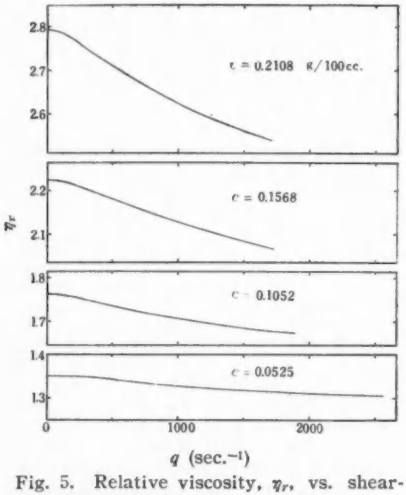

Fig. 5. Relative viscosity, η_r, vs. shear-rate, q, for F 4.

In the usual viscometry carried out by the ordinary Ostwald-type viscometer, measurements are made at constant shearing *stress* rather than at constant q by operating the viscometer at a standard driving pressure[24]. Moreover, it is customary to calculate η_r according to $\eta_r=t/t_0$ which is only the apparent η_r owing to the neglect of the second term in the bracket of Eq. (6). Accordingly, it is

24) Strictly speaking, driving pressure is not constant owing to small differences of densities amongst solutions and solvent.

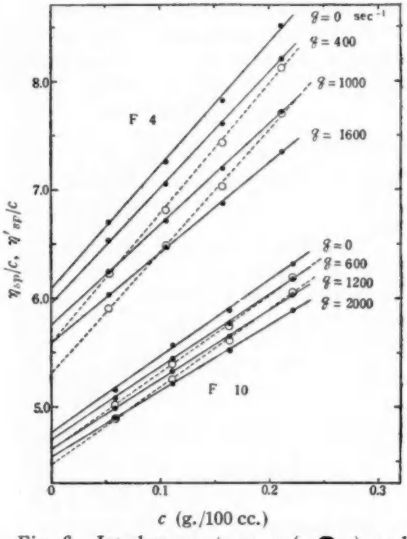

Fig. 6. Iso-shear η_{sp}/c vs. c (—●—) and iso-stress η_{sp}'/c vs. c (- - -○- - -) for F 4 and F 10. The upper iso-stress curve for each fraction is for τ=9.4 dyn./cm² and the lower for τ=18.8 dyn./cm².

pertinent to find η_{sp}/c vs. c relation at constant stress using $\eta_r'=(Pt)/(Pt)_0$ at constant P in order to see the influences of non-Newtonian behavior on the results of the usual viscometry. Some of these curves thus obtained, η_{sr}'/c vs. c, are inserted in Fig. 6 for the convenience of comparison, where shearing stress τ was calculated by the equation:

$$\tau=PR/2L \qquad (7)$$

which is the expression for the maximum stress at the capillary wall.

It can be seen from Fig. 6 that the tangent of iso-stress η_{sp}'/c vs. c curve is always larger than that of iso-shear η_{sp}/c vs. c curve. This means that Huggins' constant k' evaluated

from the data of the usual viscometry is generally greater than that from iso-shear η_{sp}/c vs. c relation except when τ is zero when the shear effect is appreciable. This is merely the natural consequence of the fact that q increases as the concentration of solution is decreased owing to the decrease in viscosity when τ is kept constant.

$[\eta]_q$ and $[\eta]_\tau$, obtained by linear extrapolation of these η_{sp}/c vs. c and η_{sp}'/c vs. c relations respectively to $c=0$, are shown in Fig. 7 as a function of q and τ, respectively.

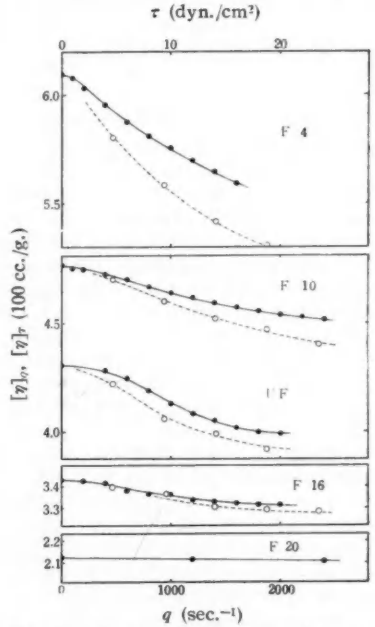

Fig. 7. $[\eta]_q$ vs. q (—●—) and $[\eta]\tau$ vs. τ (- - -○- - -). For the upper abscissa, τ, see Eq. (7).

It can be easily shown[2] that the dependence of shear-viscosity relation on MW distribution cannot take place if the shear dependence of viscosity is proportional to the first power of MW. Thus the existence of the effect of MW distribution on shear dependence such as has been noted above suggests a non-linear dependence of shear effect on MW, and in fact this seems to be brought out in Fig. 8, which shows $[\eta]_q-[\eta]_0$ and $[\eta]_\tau-[\eta]_0$ as a function of MW for a few values of q and τ.

k'_q and k'_τ, obtained from the slopes of η_{sp}/c vs. c and η'_{sp}/c vs. c curves divided by the square of each intersept, respectively, appear plotted against q and τ, respectively in Fig. 9. Although the uncertainty of k' value is large owing to the sensitiveness of k' to the experimental error, it may be safely concluded

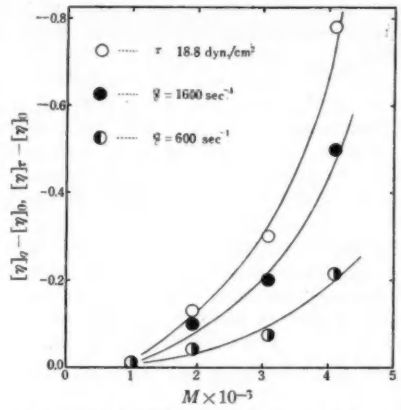

Fig. 8. $[\eta]_q-[\eta]_0$ vs. MW and $[\eta]_\tau-[\eta]_0$ vs. MW.

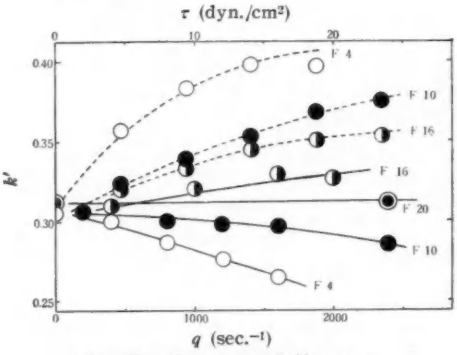

Fig. 9. k'_q vs. q and k'_τ vs. τ. For the upper abscissa, τ, see Eq. (7).

that k'_q decreases to some extent with increasing q while k'_τ increases rather rapidly with increasing τ. A small increase of k'_q with q for F 16 may simply reflect the experimental error. Fig. 10 shows k'_q and k'_τ at some values of q and τ as a function of $[\eta]_0$. It is interesting to note that $k'_{q=0}$ $(=k'_{\tau=0})$ seems to be independent on MW,

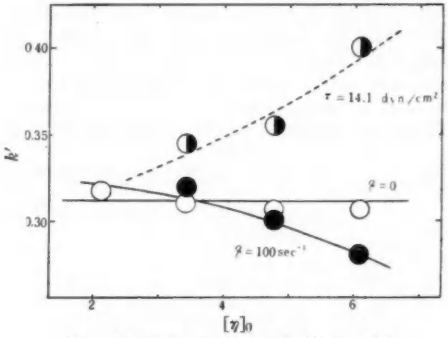

Fig. 10. k'_q vs. $[\eta]_0$ and $k'\tau$ vs. $[\eta]_0$.

while k'_q at finite q decreases slowly and k'_τ at finite τ remarkably increases as MW is increased.

The relations between $[\eta]_\tau$ and MW are shown in log-log plot for $\tau=(q=)0$ and for $\tau=18.8$ dyn./cm² in Fig. 11. For the present case, reliable determinations of K and α in $[\eta]=KM^\alpha$ as a function of τ may be hampered by the small number of fractions measured and by the possible effect of MW distribution on shear dependence of $[\eta]$ mentioned above. These results of Fig. 11 may be sufficient only to get a rough idea of the relation between α and τ. The tangents of these two lines drawn in Fig. 11 are 0.74 and

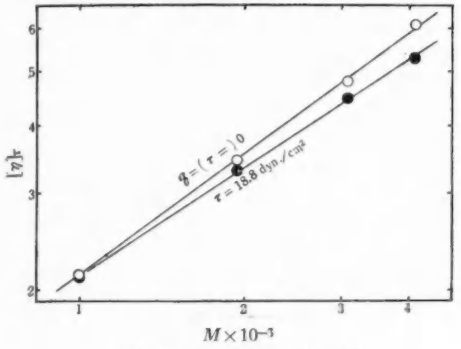

Fig. 11. $\log[\eta]_\tau$ vs. $\log M$.

0.66, respectively.

Turning to the comparison with the theory, $[\eta]_q/[\eta]_0$ of these fractions are plotted against ξ, which was calculated for each fraction by the use of Eq. (4) putting $m=104$ and $\eta_0=0.552\times10^{-2}$ poise, as shown in Fig. 12. The theoretical dependence of $[\eta]_q/[\eta]_0$ for $B\gg\lambda\eta_0L$ as given by Eq. (3) is represented by the broken line in Fig. 12.

As may be seen from Fig. 12, the tendency for $[\eta]_q/[\eta]_0$ vs. ξ relation to approach to the theoretical curve for $B\gg\lambda\eta_0L$ with decreasing MW of the polymer cannot be observed for the present case, which is not in line with what would be expected from the theory of Kuhn and Kuhn mentioned above. This should not seem, however, to be regarded as a conflict with the theory.

Kuhn and Kuhn[25] have suggested on the

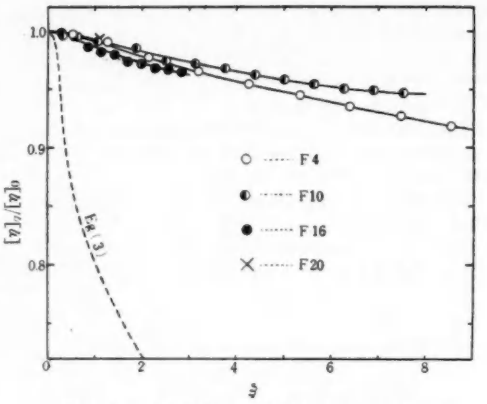

Fig. 12. $[\eta]_q/[\eta]_0$ vs. ξ for the fractions.

basis of the results of streambirefringence measurements by Signer and Gross, that the inner viscosity of a polystyrene molecule is fairly small already at MW of 44×10^4. And in this region of such high MW as have been studied in this work, the inner viscosity may be significantly small as would be expected from the theoretical relation $B\propto1/M$. The same information regarding the stiffness of the polymer molecule may be obtained from the fact that all the experimental curves lie near to the curve $[\eta]_q/[\eta]_0=1$ being apart from the theoretical curves in Fig. 12.

The apparent disaccord with the theory may be merely due to the fact that the further decrease in B with increasing MW from the order of 100×10^4 to higher values can cause only an indistinguishable change in $[\eta]_q/[\eta]_0$ vs. ξ relation within experimental error.

It appears that, in order to make a more critical test of the theory, the similar measurements should be made in the range of lower MW and over a wider range of q or on polymer of more stiff nature.

This author should like to express his gratitude to Prof. S. Murahashi and Prof. S. Akabori of this university for their kind encouragements and to Prof. W. Kuhn of the University of Basel for his kind instruction and information.

The financial asistance of the Tekkōsha Company is also gratefully acknowleged.

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25) W. Kuhn and H. Kuhn, *Ergeb. exakt. Naturwiss.*, 25, 8 (1951).

Magnetochemical Study of Nitroso Compounds

By Yoshio MATSUNAGA

(Received July 16, 1956)

Introduction

Since the early investigation of Pascal[1], little attention has been paid to the magnitude of diamagnetic susceptibility of nitroso compounds. Pascal treated the nitroso group as equivalent to the carbonyl group, and assigned +3.46[2] for the constant of the oxygen atom in the former group. But his value was supported by measurements on three compounds only, namely nitrosobenzene, N-nitrosopiperidine, and N-nitrosodiethylamine. Since nitroso compounds show deep color and a tendency to form dimer, some authors[3] proposed a triplet structure to the nitroso group. Although Wilson[4] found nitrosobenzene and *p*-nitrosodimethylaniline to be diamagnetic and did not accept the above-mentioned suggestion, he did not give any value of susceptibility of these two compounds. Farquharson[5] examined the susceptibility of nitrosobenzene, as a solid, as a melt and as a solute in benzene and acetic acid. His results showed that this compound is less diamagnetic in a molten or dissolved state than in a solid state.

It seems of interest to measure the susceptibility of some nitroso compounds, both in solid and dissolved states, in order to test the validity of Pascal's constant for the oxygen atom in the nitroso group, and to throw further light on the extraordinary change of diamagnetism found by Farquharson.

Experimental

Materials.—Nitrosobenzene[6], recrystallized from ethanol, m.p. 66–67°C. *p*-Nitrosotoluene[7], from ethanol, m.p. 48.5–49.5°C. *p*-Nitrosodimethylaniline[8], from petroleum ether, m.p. 87.5–88°C. *p*-Nitrosodimethylaniline hydrochloride[8], prepared from purified free base and hydrochloric acid, m.p. 177°C (decomp.). *p*-Nitrosodiethylaniline[9], from petroleum ether, m.p. 87.5°C. *p*-Nitrosonitrobenzene[10] from ethanol, 119–120°C. *m*-Nitrosonitrobenzene[10], from ethanol, m.p. 89–90°C. 2-Methyl-2-nitrosopropane, provided by Dr. F. Iimura, used without further purification. N-Nitrosodiethylamine[11], b.p. 170–170.5°C/756 mmHg. n_D=1.4412 at 13.0°C. N-Nitrosodiphenylamine[12], from ligroin, m.p. 68.5–69.5°C. *p*-Benzoquinone[13], sublimed in vacuum, m.p. 114°C. *p*-Nitrosophenol[14], from toluene, m.p. 124°C (decomp.). *α*-Naphthoquinone[15], sublimed in vacuum, m.p. 124°C. *α*-Nitro-*α*-naphthol[16], from ethanol, m.p. 190°C (decomp.). *β*-Naphthoquinone, commercial product, used without further purification, m.p. 125–130°C (decomp.). *β*-Nitroso-*α*-naphthol[16], from ethanol, m.p. 146–148°C (decomp.). *α*-Nitroso-*β*-naphthol[17], from ligroin, m.p. 109°C.

Magnetic Measurement.—The measurements were carried out by the Gouy method as previously described[18], using two specimen tubes, a small one (ca, 0.32 cc.) for solid specimens and a large one (ca. 1.20 cc.) for liquids. For some compounds, the susceptibility was also determined by measuring the susceptibility of the solution, and assuming that the additivity law holds for the constituents of the solution. The following solvents were used for this purpose, acetic acid ($\chi=-0.534$), dioxan (−0.570), toluene (−0.716), and concentrated hydrochloric acid (−0.675).

Results and Discussion

In Table I are presented molecular weight, and specific and molar susceptibilities for the specimens of C- and N-nitroso compounds measured, together with the values calculated by Pascal's constants for the molar susceptibility. In the cases of C-nitroso compound, the observed values of molar susceptibility are in serious disagreement with the calculated ones. For the estimation of constant of the oxygen atom in nitroso group, Pascal used nitrosobenzene alone as an example of this series of compounds, and his value is appreciably less diamagnetic than those presented by Farquharson and by us, therefore the calculated values for C-nitroso compounds have no meaning except for the convenience of the following discussion.

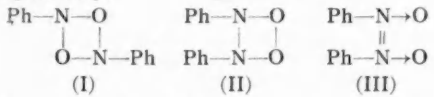
1) P. Pascal, *Bull. soc. chim. France*, **9**, 336 (1911).
2) Susceptibility values have been multiplied by 10^6 throughout this paper.
3) L. Pauling, *J. Am. Chem. Soc.*, **53**, 3225 (1931) and references cited there.
4) E. B. Wilson Jr., ibid., **56**, 747 (1934).
5) J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).
6) "Organic Syntheses", (1945), **25**, 80.
7) E. Bamberger and A. Rising, *Ann.*, **316**, 257 (1901).
8) A. Baeyer and H. Caro, *Ber.*, **7**, 963 (1874).
9) "Organic Syntheses", Coll. Vol., (1943) **2**, 223.
10) E. Bamberger and R. Hübner, *Ber.*, **36**, 3803 (1903).
11) A. Geuther, *Ann.*, **128**, 151 (1863).
12) E. Fischer' ibid., **190**, 67 (1878).
13) "Organic Syntheses", Coll. Vol., (1948) **1**, 482.
14) J. L. Bridge, *Ann.*, **277**, 79 (1893).
15) C. E. Groves, *J. Chem. Soc.*, **26**, 209 (1873).
16) R. Henriques and M. Ilinski, *Ber.*, **18**, 704 (1885).
17) "Organic Syntheses", Coll. Vol. (1948) **1**, 411.
18) H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

TABLE I

DIAMAGNETIC SUSCEPTIBILITIES OF NITROSO COMPOUNDS

Substance	M.w.	Suscept. ($-\chi$)	Molar Suscept. ($-\chi_M$) Obs.	Calcd.	Lit
Nitrosobenzene	107	0.552	59.1	54.2	55.0[1] 60.2[5]
p-Nitrosotoluene	121	0.582	70.4	66.1	—
p-Nitrosodimethylaniline	150	0.489	73.3	86.4	—
p-Nitrosodiethylaniline	178	0.520	92.6	110.1	—
p-Nitrosonitrobenzene	152	0.433	65.8	60.5	—
m-Nitrosonitrobenzene	152	0.434	66.0	60.5	—
N-Nitrosodiethylamine	102	0.581	59.3	61.0	60.6[1]
N-Nitrosodiphenylamine	198	0.559	110.7	111.9	—

As it is well known that nitrosobenzene exists as dimeric form in the solid state, the calculated molar susceptibility must be computed for this structure. But the structure of dimeric nitrosobenzene has not been determined yet. Ingold and Piggott[19] and Pauling[3] suggested the structure (I) containing the nitrogen-oxygen ring which is analogous to that of dimeric nitric oxide[20]. On the other hand, the chemical evidence favors the structure in which nitrogen atoms are bound together, and Stewart[21] and Hammick[22] proposed the structures (II) and (III) respectively.



(I) (II) (III)

The same apparent molar susceptibility is computed by Pascal's law to be -58.2 or -60.2 for the structures (I) and (II), using the constitutional correction constant for four-membered carbon ring $+3.05$[23] or $+1.1$[24] instead of the unknown one for nitrogen-oxygen ring. For the structure (III), -59.2 is estimated from the observed value for azobenzene -105.3[25] with the aid of the system of Gray and Cruickshank[25]. All of these calculated molar susceptibilities are in good agreement with the observed one, and we cannot decide the most probable one among these three structures. The differences between the observed and calculated molar susceptibilities of *p*-nitrosotoluene, and *m*- and *p*-nitrosonitrobenzenes can be interpreted similarly, but those of *p*-nitrosodialkylanilines, which are less diamagnetic than the calculated values in contrast with the above-mentioned cases, must be considered further.

In the dissolved state, nitrosobenzene and its derivatives are blue or green, and cryoscopic data[22] show that they exist mainly as monomeric form. As *p*-nitrosodialkylanilines are green even in the solid state, they have certainly the nitroso group which is chromophoric, and the depression of diamagetism may be attributed to this distinctive character. With the purpose of confirming this view we examined the susceptibility of the solution, and the values of these compounds were calculated by the direct application of Wiedemann's additivity law. The results are in Table II, with the calculated molar susceptibilities given by Pascal's constant for nitroso group.

It should be noted that the observed molar susceptibilities are from 10 to 18 units less diamagnetic than the calculated values in all of the C-nitroso compound. The depression is also found in nitrosobutane, and we thus conclude that this depression is attributed to the presence of nitroso group attached to a carbon atom, and its magnitude is affected by the conjugation with aromatic nucleus and the other substituents. Consequently, the magnetic contribution of the nitroso group as a whole in these compounds is paramagnetic of the order of 10 units. In the cases of the N-nitroso compound, the molar susceptibility does not depend on the states, i.e. solid, liquid and dissolved, and they agree with the calculated values within the accuracy of measurements and estimations. From the magnetic standpoint, it is apparent that the nitroso group attached to a nitrogen atom is unlike that attached to a carbon atom.

The paramagnetic contribution of the nitroso group found here is very weak if we compare it with that found in the substance with a permanent magnetic moment.

19) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 168 (1924).
20) W. J. Dulmage, E. A. Meyers and W. N. Lipscomb, *J. Chem. Phys.*, **19**, 1432 (1951).
21) Cited in reference 3.
22) D. Ll. Hammick, *J. Chem. Soc.*, **1931**, 3105.
23) J. Farquharson and M. V. C. Sastri, *Trans. Faraday Soc.*, **33**, 1474 (1937).
24) P. Pascal, *Compt. rend.*, **181**, 656 (1925).
25) Y. Matsunaga, This Bulletin, **29**, 308 (1956).
26) F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31**, 1491 (1935).

TABLE II

DIAMAGNETIC SUSCEPTIBILITIES OF NITROSO COMPOUNDS IN THE DISSOLVED STATE

Solute	Solvents*	No. of Detn.	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Calcd.
Nitrosobenzene	A	3	0.372		
	T	2	0.393	41.0	54.2
p-Nitrosotoluene	D	1	0.440		
	T	1	0.435	53.0	66.1
p-Nitrosodimethylaniline	T	2	0.490	73.5	86.4
p-Nitrosodiethylaniline	T	2	0.691	92.4	110.1
2-Methyl-2-nitrosopropane (Nitrosobutane)	D	1	0.489	42.5	52.5
N-Nitrosodiethylamine	D	1	0.569		
	T	1	0.587	59.0	61.0
N-Nitrosodiphenylamine	D	1	0.545		
	T	1	0.566	110	111.9

* A: acetic acid. D: dioxan. T: toluene.

Therefore, if we assume that the apparent difference is due to the partial compensation of diamagnetism by the paramagnetic contribution of triplet state, the molecule may be excited at the rate of the order of one thousandth. This assumption seems to be improbable for the following two reasons. In the first place, the excitation energy expected from the magnetic data is about 7 kcal. mol.$^{-1}$, and this is only one fifth of that suggested from the spectroscopic data[27]. In the second, the state of the substance may somewhat affect the magnitude of the excitation energy, and also the apparent paramagnetic contribution of the nitroso group. But *p*-nitrosodialkylanilines do not show such a tendency[28]. In another explanation of the contribution of the nitroso group, we must consult Van Vleck's equation[29] for the molar susceptibility of a polyatomic molecule with no resultant electron spin moment, namely,

$$\chi_M = -\frac{Ne^2}{6mc^2}\sum r^2 + \frac{2}{3}N\sum_{n'\neq n}\frac{|m^0(n';n)|^2}{h\nu(n';n)}$$

where $m^0(n';n)$ is a non-diagonal element of the matrix for the angular momentum of the system, $\nu(n';n)$ is the frequency corresponding to $n';n$ transition, and the other terms have their usual physical significance. If the second term is dominant in the nitroso group, the magnetic contribution of this group as a whole may be feebly paramagnetic and independent of temperature. Such examples are not rare in inorganic compounds, but in organic compounds, the second term is usually smaller than the first one, and the case found here is very striking. However, we wish to emphasize that there is no essential difference between diamagnetism and temperature-independent paramagnetism, and the sign of the susceptibility depends only on the magnitude of these two terms.

TABLE III

DIAMAGNETIC SUSCEPTIBILITIES OF QUINONES AND THEIR MONOXIMES

Substance*	M. w.	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Diff**	Lit.
p-Benzoquinone	108	0.355	38.4	—	41.3[30], 40.0[31], 38.2[32], 34.4[33]
p-Nitrosophenol	123	0.412	50.7	12.3	50.3[1]
α-Naphthoquinone	158	0.465	73.5	—	73.8[21], 73.0[33],
α-Nitroso-*α*-naphthol	173	0.530	91.8	18.3	—
β-Naphthoquinone	158	0.430	67.9	—	—
β-Nitroso-*α*-naphthol	173	0.478	82.7	14.8	—
α-Nitroso-*β*-naphthol	173	0.485	83.9	16.0	—

* Monoximes are indicated by the name of isomeric nitrosophenol.
** Monoxime (obs.) −Quinone (obs.).

27) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **67**, 994 (1945).
28) The validity of this assumption was completely denied. According to Dr. I. Miyashita, Hokkaido University, *p*-nitrosodialkylanilines do not show paramagnetic absorption (private communication).
29) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Oxford University Press, Oxford (1932), p. 275.
30) P. Pascal, *Bull. soc. chim. France*, **9**, 177 (1911).
31) K. S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc.*, **A234**, 265 (1935).
32) H. Mikhail and F. G. Baddar, *J. Chem. Soc.*, **1944**, 590.
33) E. D. Bergmann et al., *J. chim. phys.*, **49**, 474 (1952).

Pascal concluded that nitrosophenol exists as quinone monoxime in the crystal, comparing its molar susceptibility to the calculated value using his own constants. However, as already shown, owing to the paramagnetic contribution of nitroso group it seems to be difficult to decide whether the magnitude of molar susceptibility favors the quinone monoxime form. We measured also some of quinone monoxime, and the values are compared with those of the parent quinones. The results are presented in Table III. The values of the molar susceptibility increment associated with the transition $>C=O \rightarrow >C=N-OH$ markedly depend on the nature of the rest of the molecule, and they are more diamagnetic than those found in the aliphatic series which were reported as from 7.4 to 11.7 units[34]. Hence it appears that the oxime group cannot localize π-electrons in the aromatic nucleus so strongly as carbonyl group, and the evaluation of the molar susceptibility of quinone monoxime by a set of constants is difficult.

(V)

The possible other structure is (V), in which the hydrogen ion is attached to the oxygen atom in the nitroso group. The expected values for this stucture are somewhat obscure, because the most similar compound the susceptibility of which is known is quinone monoxime, and the substitution of carbonyl group by $>C=NR_2$ may affect the degree of localization of aromatic electrons. If the transition $>C=O \rightarrow >C=NR_2$ does not affect the magnetic contribution of aromatic electrons, the value B_1 may be expected, and if the delocalization occurs in this transition again to a similar extent to that found in the transition from quinone to its monoxime, the value B_2 may be expected. The observed values are in the expected ranges, and seem to be consistent with the structure (V).

Summary

The magnetic susceptibility of nine nitroso compounds, as solids and as solutes, were measured by the Gouy method. The constant for the nitroso group attached to a carbon atom was found to be paramagnetic of the order of 10 units. The author suggested that the second term in Van Vleck's equation for the diamagnetism of a molecule is dominant in this case. Some quinones and their monoximes were also measured, and it appeared that the ability of the oxime group to localize aromatic electrons is less than that of the carbonyl group. In addition, the structure of nitrosodialkylaniline hydrochloride was discussed from the magnetic standpoint.

TABLE IV

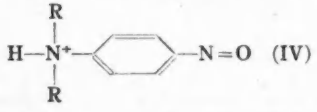
DIAMAGNETIC SUSCEPTIBILITIES OF *p*-NITROSODIALKYLANILINE HYDROCHLORIDES

Ion	Molar Suscept. ($-\chi_M$) Obs.	Calcd.			
		A_1	A_2	B_1	B_2
p-Nitrosodimethylaniline+H^+	79.9*	73.9	93.0	77.0	82.7
p-Nitrosodiethylaniline+H^+	101**	93.2	116.7	100.7	106.4

* Hydrochloride (103.3) −Chloride ion (23.4)[35].

** Apparent susceptibility of free base in hydrochloric acid solution.

Nitrosodialkylanilines form the salts with inorganic acids, and the color change from green to yellow suggests the disappearence of the distinctive nature of the nitroso group. In order to elucidate the structure of the cation, we examined their susceptibilities measuring the susceptibility of the crystalline salt or the hydrochloric acid solution. The observed values shown in Table IV will be compared with the calculated values of some of the models of the cation. The value A_1 is for the monomeric anilinium ion (IV), and the value A_2 for the dimer. However, the former computed on the basis of the observed susceptibility for the free base is too small and the latter given by Pascal's law is too large.



(IV)

The author wishes to express his hearty thanks to Prof. H. Akamatu for his kind direction, and to the late Dr. F. Iimura for a sample of nitrosobutane. The cost of this study has been defrayed from the Grant in Aid for Scientific Research from the Ministry of Education, to which the author's thanks are also due.

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34) C.M. French and D. Harrison, *J. Chem. Soc.*, 1955, 3513.

35) V. C. G. Trew, *Trans. Faraday Soc.*, **37** 476 (1941).

The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds. II[1]

By Makoto TAKAHASI

(Received August 9, 1956)

The mechanism of the reactions of the mixture of hydrogen bromide and oxygen with various ethenoid compound has been studied by many workers, and its main character has been elucidated as follows:

(1) $\rangle C=C\langle + O_2 + HBr \longrightarrow Br\cdot$ (initiation)

(2) $\rangle C=C\langle + Br\cdot \longrightarrow \rangle \dot{C}-C\langle_{Br}$ (propagation)

(3) $\rangle \dot{C}-C\langle_{Br} + O_2 \longrightarrow \rangle C-C\langle_{\cdot O_2}^{Br}$ (propagation)

(4) $\rangle C-C\langle_{\cdot O_2}^{Br} + HBr \longrightarrow \rangle C-C\langle_{HO_2}^{Br} + Br\cdot$ (propagation)

(5) $\rangle C-C\langle_{HO_2}^{Br} + HBr \longrightarrow$ inert product $+ Br\cdot$ (propagation)

(6) $Br\cdot + Br\cdot \longrightarrow Br_2$ (termination)

(7) $\rangle \dot{C}-C\langle_{Br} + Br\cdot \longrightarrow \rangle C-C\langle_{Br}^{Br}$ (termination)

Although the mechanism of the abnormal addition of hydrogen bromide to ethenoid compounds has been established by several workers, the oxidation reaction of ethenoid compounds with oxygen in the presence of hydrogen bromide has not yet been completely elucidated. The mechanism represented above involves several problems to be solved:

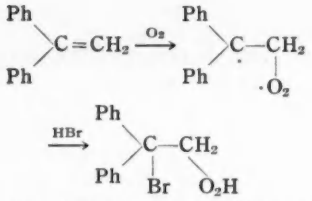
(1) The initiation process has been assumed to start by the interaction of an ethenoid compound with hydrogen bromide and oxygen, but it does not mean that a triple collision takes place actually. The process may be composed of at least two steps, but it is not yet determined whether oxygen reacts first with the ethenoid compound and then with hydrogen bromide or vice versa. Consideration of the autoxidation reaction of ethenoid compounds (in the absence of hydrogen bromide) leads to an assumption that oxygen reacts first with the ethenoid compound. But the mechanism of the initiation reaction of autoxidation itself is not clearly known in spite of many discussions. L. Bateman[2] pointed out that the direct olefin-oxygen reaction is so slow that it cannot be hoped that examination of the oxidation product may provide any information on any non-hydroperoxide initiation in the absence of a large amount of inhibitors. The situation, however, is here a little different, because many olefins investigated by the present author have no α-methylene group, so that the oxygen molecule acts on π-electrons of the double bond. Moreover, if the initiation reaction and the propagation reaction give different kinds of products (and the latter a large amount), they may be distinguished by an appropriate analytical method. It is also possible that the ethenoid compound reacts first with hydrogen bromide to form a loose molecular complex, because hydrogen bromide increases the solubility of ethenoid compounds in solvents such as benzene and carbon tetrachloride and there is certain evidence for the formation of complex compounds from aromatic compounds and hydrogen chloride[3].

The formation of small amounts of carbon dioxide and diphenylbromomethane in the reaction of diphenylethylene with hydrogen bromide and oxygen appears to be helpful to the elucidation of the reaction of ethenoid compounds with hydrogen bromide and oxygen. The three following ways of explanation may be possible for the mechanism of the formation of carbon dioxide and diphenylbromomethane. (a) Carbon dioxide and diphenylbromomethane may be formed by an initiation reaction, but not by a propagation reaction. If it is the case, oxygen acts first on the β-carbon atom of diphenylethylene to give $Ph_2\dot{C}-CH_2(O_2)$ rather than on the α-carbon atom to give $Ph-\dot{C}(\cdot O_2)-CH_2$, and the reaction proceeds in the following way:

1) Part I, This Bulletin, 29, 625 (1956).

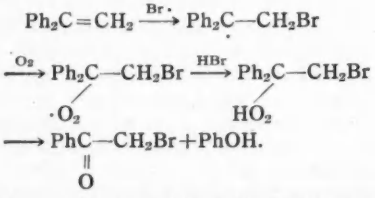
2) L. Bateman, *Quart. Rev.* VIII, 147, (1954).

3) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 74, 3572 (1952).



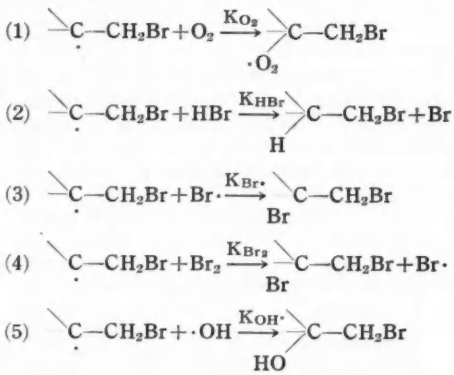
The bromohydroperoxide may decompose to carbon dioxide and diphenylbromomethane through a not yet characterized process in the presence of oxygen and hydrogen bromide. (b) The products are produced by the initiation process as above. But the olefin may form an intermediate complex with oxygen*, and then the complex reacts with hydrogen bromide:

(c) An alternative assumption might be that these products were produced by a propagation reaction, but it is probably far from the fact because diphenylethylene adds the bromine atom at the β-carbon atom more rapidly than at the α-carbon atom due to the stability of $Ph_2\dot{C}-CH_2Br$ greater than that of $Ph_2BrC-\dot{C}H_2$. The formation of ω-bromoacetophenone and a phenolic compound in relatively large amounts in the reaction may be explained by assuming a propagation reaction as follows:



The author considers that the assumptions (a) and (b) are more probable than (c). The decomposition of hydroperoxides (e.g. $Ph_2C(HO_2)-CH_2Br$) by hydrogen bromide has not been studied in detail until the present, but it may probably proceed through an acid catalysed mechanism, as suggested by F. F. Rust and W. E. Vaughan[4]. The formation of phenolic substances from diphenylethylene and from styrene is explained by this mechanism.

(2) It is impossible to establish completely the scheme of the propagation, chain transfer and termination reactions from the result of the yield of the final products, because the velocity constants of the following most probable competitive processes have not yet been estimated in any case:



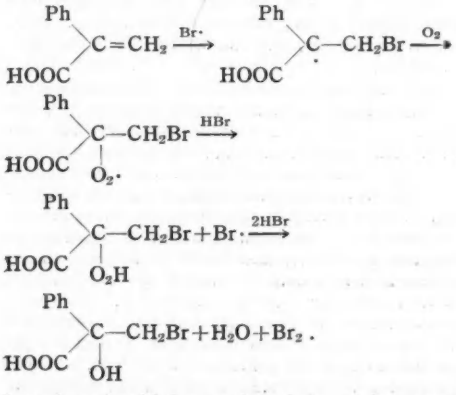
Generally. the velocity constants of the recombination reactions of the free radical with the bromine atom (3) and with the free hydroxyl radical (5) may be far greater than those of the reactions of the free radical with molecular oxygen (1), with hydrogen bromide (2), and with bromine molecule (4), unless some steric effect modifies the velocity constants, but the concentrations of the bromine atom and of the free hydroxyl radical may be far smaller than those of oxygen, hydrogen bromide and molecular bromine. Although atropic acid gives a large amount of α-hydroxy-β-bromohydratropic acid, it is improbable from the reason stated below that the product is yielded by the reaction of free radical $PhC(HOOC)-\dot{C}H_2Br$ with free hydroxyl radical. A comparison of the velocity constants of the reactions (1), (2) and (3) is also impossible now. It seems probable that the reactivity of the free radical with hydrogen bromide depends upon the stability of the free radical, and that the velocity constant K_{O_2} is in general greater than K_{HBr}, considering that many compounds such as cinnamic acid, atropic acid, and diphenylethylene, which give free radicals stabilized by conjugation, give various oxygenated compounds but not hydrogen bromide adducts in spite of the presence of a large amount of hydrogen bromide. The comparison of the velocity constants K_{O_2} and K_{HBr} has an important meaning in considering the reaction mechanism discussed here. It is known that the bromine addition reaction of cinnamic acid is inhibited by the presence of oxygen,

* There is an indication that aromatic compounds form complex compounds with oxygen. D. F. Evans, *J. Chem. Soc.*, 1953, 345.

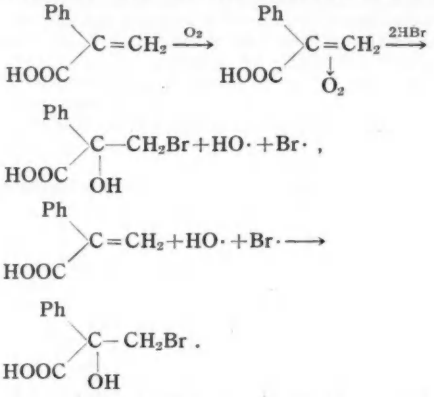
4) R. R. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **41**., 2595 (1949).

but the inhibition seems not to be serious according to our experiment described in the next paper.

In the previous paper[1] the author emphasized the significance of the material balance in order to discuss the reaction mechanism. Unfortunately, in many cases of the reactions discussed by the author such as those of crotonic acid, diphenylethylene and stilbene, the reaction mixtures are composed of several compounds, which are relatively labile to chromatography, recrystallization and distillation, so that the establishment of the material balance is unsuccessful. Fortunately, in the reaction of atropic acid with hydrogen bromide and oxygen, α-hydroxy-β-bromohydratropic acid (the determination of the structure of the acid is described in the experimental part) was obtained in about 77 mole percent yield of atropic acid. In addition to this a very small amount of ω,ω-dibromoacetophenone and carbon dioxide and bromine were obtained. These products may be derived by the initiation reaction or a side reaction, but the details of the mechanism is not clear. Atropic acid which gives neither a hydrogen bromide adduct nor atropic acid dibromide is clearly distinguished from cinnamic acid giving more than fifty mole percent of cinnamic acid dibromide and about 25 mole percent of ω-bromoacetophenone under the same conditions. If α-hydroxy-β-bromohydratropic acid was formed by the following process,

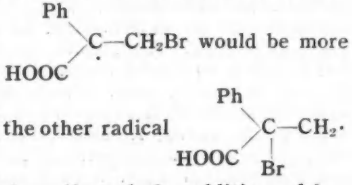


bromine should be produced in moles equal to α-hydroxy-β-bromohydratropic acid, but actually only a small amount of free bromine, no appreciable amount of water, and no atropic acid dibromide is found in the reaction products. The necessary condition in considering the reaction mechanism is that the atom which adds first to double bond should attack the β-carbon atom of atropic acid, but not the α-carbon atom, because of the greater stability of the free radical formed. Then the following may be a possible mechanism, which involves no cyclic chain propagation:



The problem, however, will be left unsolved until a kinetic study of these reactions is possible.

G. Merling[5] asserted, that atropic acid gave β-bromohydratropic acid with hydrobromic acid, while α-bromohydratropic acid was obtained when dry hydrogen bromide was passed through a benzene solution of atropic acid. If such a reversal of the direction of addition of hydrogen bromide to atropic acid should take place, it could not be explained on the grounds of the formation of the more stable free radical in the of reaction of bromine atom with the olefinic compound, because



the radical would be more stable than the other radical

The author investigated the addition of hydrogen bromide to atropic acid both under oxydant and anti-oxydant conditions, but no reversal was observed.

Experimental

Materials.—Hydrogen bromide and oxygen were prepared and purified as described in the previous paper[1]. Diphenylethylene was prepared from bromobenzene and ethyl acetate according to Org. Syntheses[6], b. p. 123–5°C/mmHg, $n_D^{19^\circ}$ 1.6084, $n_D^{9.6^\circ}$ 1.6135. Atropic acid was prepared by the hydrolysis of acetophenone cyanohydrin and recrystallized from benzene, m. p. 106°C. Styrene, a

5) G. Merling, *Ann.*, **209**, 1 (1881).
6) "Organic Syntheses", Collective Vol. I, John Wiley & Sons, Inc., p. 221.

commercial product, was washed with alkaline water, dried with calcium chloride and distilled under reduced pressure with a fractionation column.

Reaction of Diphenylethylene with Hydrogen Bromide and Oxygen.—The mixture of hydrogen bromide and oxygen was passed into a solution of diphenylethylene in benzene or in carbon tetrachloride for several hours. The results of experiments under various conditions are summarized in Table I and details will be described below. a) Identification of diphenylbromomethane. The reaction mixture of Exp. 1. was washed with water, and dried with anhydrous sodium sulfate. When benzene was removed by distillation, a light yellow oil was obtained. The oil was heated with a few ml. of water in a sealed tube at 150°C for about four hours. After cooling, the sealed tube was opened, and a mixture of an oil and a crystalline mass was obtained. The crystalline mass was separated and recrystallized from petroleum ether, m.p. 120°C. It contained no bromine and was identified as dibenzhydrylether $((C_6H_5)_2CH)_2O$ by a mixed melting point. The authentic dibenzhydrylether was synthesized from diphenylbromomethane by heating it with water in the same way. An attempted separation of diphenylbromomethane itself in Expt. 6 by distillation under reduced pressure was rendered unsuccessful by the presence of a large amount of unchanged diphenylethylene. b) Identification of ω-bromoacetophenone. In Expt. 5 the oil was kept in an electric refrigerator, giving a mixture of an oil and a crystalline mass. The crystalline mass was separated on a glassfilter, and weighed about 0.4 g., m.p. 52°C., and it was identified as ω-bromoacetophenone, by a mixed melting point and by the preparation of 2,4-dinitrophenylhydrazone, m.p. 214–216°C. d) Identification of phenol. When the reaction mixture was shaken with water or alkaline water, and a bromine-potassium bromide solution was added to the aqueous extract, tribromophenol was precipitated. Furthermore, when the alkaline extract was saturated with carbon dioxide and extracted with ether, about 2 g. of a phenolic oil were obtained. From the oil about 1.45 g. of phenyl benzoate was obtained by treating it with benzoyl chloride (Expt. 7). Unfortunately, the separation of these products from the reaction mixture of one experiment using 10 g. of diphenylethylene was unsuccessful. When 10 g. of diphenylethylene were used, the feature of the reaction was a little different. (Expt. 6 and 7) The amount of carbon dioxide was nearly in the same order. When the carbon tetrachloride solution was shaken with 1 N NaOH solution once and with 100 ml. of distilled water dried with anhydrous sodium sulfate, and distilled under reduced pressure, it gave the three following fractions, b.p. 82–85°C/0.9 mmHg, and 100°C/1 mmHg and the residue. The first fraction ($n_D^{9.5}$ 1.6182) contained no bromine and was found to be mainly composed of unchanged diphenylethylene, ($n_D^{9.5}$ 1.6135). The second fraction solidified and was recrystallized from petroleum ether, m.p. 38°C.

Anal. Found: Br, 30.9. Calcd. for $(C_6H_5)_2CCHBr$: Br, 30.9%.

These results suggest that a large amount of diphenylethylene does not react with the mixture of hydrogen bromide and oxygen due to the accumulation of a phenolic substance in the reaction mixture. β-Bromodiphenylethylene may be derived from α, β-dibromodiphenylethane during distillation, for the latter is very sensitive to heat.

Reaction of Atropic Acid with Hydrogen Bromide and Oxygen.—Experimental results are summarized in Table II. Expt. 59 was carried out as following: Atropic acid (5 g., 0.034 mol.) was dissolved in 50 ml. of carbon tetrachloride and the mixture of hydrogen bromide and oxygen was passed into the solution for 300 min. at room temperature. The solution turned red during the reaction. It was kept over-night in an electric refrigerator, giving 2 g. of a crystalline mass, which was recrystallized from benzene to colorless crystals, m.p. 115°C. The substance was acidic, and found to be α-hydroxy-β-bromohydratopic acid as described below.

The carbon tetrachloride solution was washed twice with distilled water, and the aqueous solution was extracted with ether. The ethereal extract gave about 2 g. of the same acid, m.p.

TABLE I

THE REACTION OF DIPHENYLETHYLENE WITH HYDROGEN BROMIDE AND OXYGEN

No.	Diphenylethylene g. (mol.)	Solvent ml.	Reagents	Time Min.	Products: CO_2 mm. mol.	Ph_2CHBr	$PhCOCH_2Br$	PhOH mm. mol.	Ph_2CBrCH_2Br	$Ph_2C=CH_2$
1	2(0.011)	Benzene 70	$HBr+O_2$	180	0.9	+	Not investigated	Not investigated	?	?
2	2	〃 30	〃	70	0.7		Purification unsuccessful			
3	2	〃 30	〃	105	0.8	+	?	?	?	?
5	3.51(0.0195)	〃 40	〃	100	0.6	?	?	5	?	+
6	10(0.0056)	CCl_4 70	〃	215	0.6	?	?	6	?	+
7	10	〃 70	〃	360	0.8	?	?	7	+	+

"?" Means that its existence was not ascertained, but it is most probable.
"+" Means that its existence was ascertained qualitatively.
"–" Means that its absence was ascertained.

TABLE II

THE REACTION OF ATROPIC ACID WITH HYDROGEN BROMIDE AND OXYGEN

No.	Atropic Acid, g. mol.	Solvent, ml.	Reagent	Reaction Time Min.	Products: CO_2 mm mol.	Br_2 mm mol.	$PhCCH_2Br$ HOOC OH mm mol.	$PhCHCH_2Br$ HOOC mm mol.	$PhCOCHBr_2$
48	1	CCl_4 30	$HBr+O_2$	230	1.3				
52	1.5 (0.01)	〃 30	N_2 HBr	60 290	None			6.5	
53	1.5	〃 30	Benzoyl Peroxide, 30 mg. HBr	295	〃			5.7	
55	5.00 (0.034)	〃 50	$HBr+O_2$	325	5.3	1.45	18		+
58	〃	〃 50	〃	300	3.5		19		+
59	〃	〃 50	〃	300	3.4	0.25	25		+
56	0.2	Benzene 20	(O_2 for a short time) HBr	180	—	—	—	Oily product	
57	0.2	〃 30	HBr Catechol 10 mg.	195	—	—	—	+	

115°C. The carbon tetrachloride solution was then shaken twice with 50 ml. of 1 N aqueous sodium hydroxide, and the alkaline solution was acidified with hydrochloric acid and extracted with ether. The ethereal extract gave about 0.9 g. of the same acid. Thus about 6.1 g. (0.026 mol. as calculated for α-hydroxy-β-bromohydratropic acid) of the acid, m. p. 115°C, was obtained from 5 g. (0.034 mol.) of atropic acid. The carbon tetrachloride solution was then dried with anhydrous sodium sulfate, and evaporated under reduced pressure, when a small amount of a precipitate and 0.94 g. of an oil were left. The oil (0.78 g. of the oil in ethyl alcohol) and 2,4-dinitrophenylhydrazine gave a precipitate weighing 0.377 g. It was separated into parts soluble and insoluble in hot chloroform. The former was a yellow crystalline substance, which melted at 178–180°C after one recrystallization from chloroform.

Anal. Found: C, 38.27; H, 2.51; N, 12.7; Br, 33.5. Calcd. for $C_{14}H_{10}O_4Br_2$: C, 36.71; H, 2.20; N, 12.2; Br, 34.9%.

The latter was an orange crystal, insoluble in any solvents available, contained no bromine, and melted at about 200°C. Its amount was very small, so that its identification was unsuccessful. ω,ω-Dibromoacetophenone itself also gave two species of products with 2,4-dinitrophenylhydrazine, which appeared to be the same substances as those obtained above. The 2,4-dinitrophenylhydrazone, m. p. 178–180°C was identified with the 2,4-dinitrophenylhydrazone of ω,ω-dibromoacetophenone by mixed melting point and by comparison of their infrared spectra as shown in Fig. 1 and 2, although the analytical results did not give a good agreement as 2,4-dinitrophenylhydrazone of ω,ω-dibromoacetophenone $C_{14}H_{10}O_4Br_2$, because the amount of the sample was so small that it could not be repeatedly recrystallized.

The acid, m. p. 115°C, had a neutralization equivalent of 244, and its composition was as follows:

Anal. Found: C, 44.9; H, 3.92; Br, 32.0. Calcd. for $C_9H_9O_3Br$: C, 44.1; H, 3.67; Br, 32.3%.

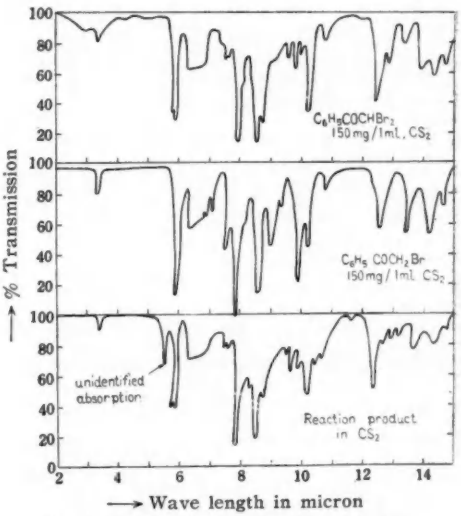


Fig. 1. Infrared spectra of two ketones and of reaction products (Expt. 59).

This indicates that the acid is either α-hydroxy-β-bromo- or α-bromo-β-hydroxyhydratropic acid. The positions of the hydroxyl group and the bromine atom were determined as follows: Infrared spectrum of the acid appeared to be similar to that of atrolactic acid as shown in Fig. 3. Treatment of the acid with Fenton reagent gave no carbonyl compound. An attempted synthesis of the acid by the reaction of atropic acid with hypobromic acid resulted in the formation of only a polymeric substance containing no bromine. However, when it was brought to reaction with lead tetracetate, it gave ω-bomoacetophenone, which resulted from the oxidative scission of α-hydroxy-β-bromohydratropic acid, because it was reported that[7], when an α-hydroxycarboxylic acid is treated with lead tetracetate, it gives a carbonyl

7) H. Oeda, This Bulletin, 9, 8 (1934).

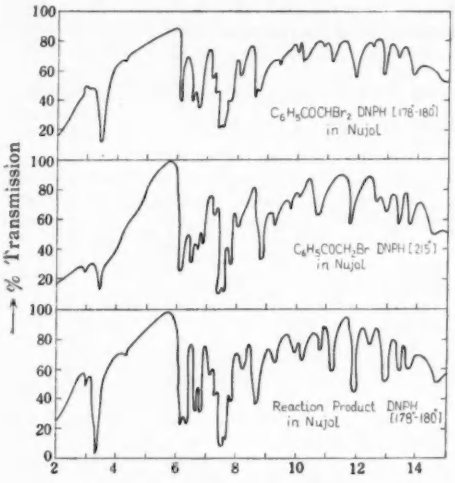

% Transmission
$C_6H_5COCHBr_2$ DNPH (176°-180°) in Nujol
$C_6H_5COCH_2Br$ DNPH (215°) in Nujol
Reaction Product DNPH (178°-180°) in Nujol
Wave length in micron

Fig. 2. Infrared spectra of 2, 4-dinitrophenylhydrazones (DNPH) of two ketones and of reaction products (Exp. 59).

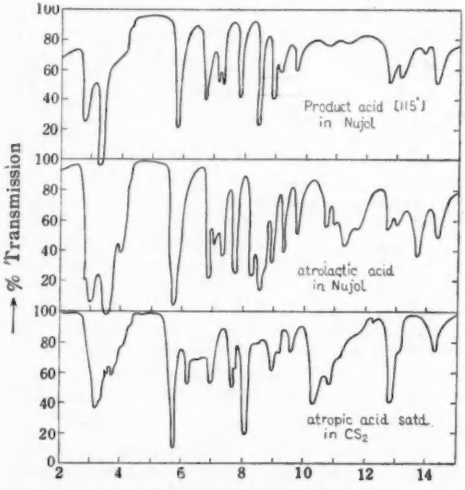
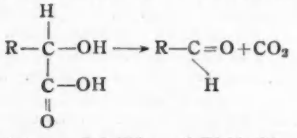


Fig. 3. Infrared spectra of α-hydroxy-β-bromohydratropic acid, atrolactic acid, and atropic acid.

compound and carbon dioxide as follows:



A mixture of 0.236 g. of $Pb(AcO)_4$ and 0.245 g. of the acid, m. p. 115°C, in 3 ml. of benzene was heated at 60–65°C. for 1.5 hr. After it was assured with a KI solution that no unchanged $Pb(AcO)_4$ remained, the yellow precipitate was filtered off. From the benzene solution a highly irritating oil was obtained on removing benzene by distillation. The oil partly solidified when it was kept in a cold place, but, as the amount was very small, the whole was brought to reaction with 2, 4-dinitrophenylhydrazine, giving an orange-colored precipitate. It was recrystallized from chloroform, m. p. 215°C.

Anal. Found: Br, 20.7. Calcd. for 2, 4-dinitrophenylhydrazone of ω-bromoacetophenone, $C_{14}H_{11}N_4O_4Br$: 21.7%.

A mixed melting point showed it was 2, 4-ninitrophenylhydrazone of ω-bromoacetophenone. From these results it was concluded that the acid was α-hydroxy-β-bromohydratropic acid, $C_3H_5C(CH_2Br)(OH)COOH$. This acid did not react with Fenton reagent, probably because of the absence of hydrogen atom at the hydroxylated carbon atom.

Addition of Hydrogen Bromide to Atropic Acid.—In 30 ml. of carbon tetrachloride 1.5 g. of atropic acid was dissolved, and hydrogen bromide was passed into the solution for 290 min. after sweeping the solution by nitrogen. A very small amount of a precipitate was obtained, which did not dissolve in various solvents and melted at 220°C. It contained no bromine and it may be a dimer of atropic acid. The solution was washed twice with distilled water, dried with anhydrous sodium sulfate, and evaporated, giving 1.5 g. of a crystalline substance, which was recrystallized from carbon disulfide, m. p. 96°C.

Anal. Found: Br, 34.1. Calcd. for $C_9H_{10}O_2Br$: Br, 34.9%.

By a mixed melting point, it was found to be β-bromohydratropic acid (Expt. 52.)

Addition of Hydrogen Bromide to Atropic Acid in the Presence of Benzoyl Peroxide.—Into a solution of 1.5 g. of atropic acid and 0.030 g. of benzoyl peroxide in 30 ml. of carbon tetrachloride hydrogen bromide was passed for 300 min. at the room temperature. By the same treatment as described above β-bromohydratropic acid was identified by a mixed melting point (Expt. 53).

The Reaction of Styrene with Hydrogen Bromide and Oxygen.—The mixture of hydrogen bromide and oxygen was passed into a solution of 10.0 g. (0.096 mol.) of styrene in 60 ml. of carbon tetrachloride for 240 min. at 20°C. The amount of carbon dioxide was 0.144 g. as barium carbonate (0.00073 mol.), and the water used to absorb waste hydrogen bromide gave a positive test with Schiff reagent, suggesting the presence of formaldehyde, although its identification was not successful. The carbon tetrachloride solution was washed with 120 ml. of 1 N NaOH, then with 60 ml. of water, and dried with anhydrous sodium sulfate. The alkaline solution was saturated with carbon dioxide, and extracted with ether. The ethereal solution gave a phenolic substance, but its identification was unsuccessful. The neutral oil obtained from the carbon tetrachloride solution was distilled under reduced pressure. The first fraction, which distilled at 58–60°C/3 mmHg weighed about 1.6 g., and was identified as α-bromoethylbenzene, by comparing the refractive index of

the oil ($n_D^{12.5}$ 1.5642) with that of an authentic specimen ($n_D^{12.5}$ 1.5636). The second fraction distilled at 108–110°C/3 mmHg and about 2.3 g. of the distillate solidified and showed a melting point 65°C.

Anal. Found: Br, 61.1. Calcd. for styrene dibromide, $C_8H_8Br_2$: Br, 60.7%. The total amount of styrene dibromide obtained in crystals in this experiment was not less than 4.8 g. (2.3+1.8+0.7). Supposedly the oil separated from the solid styrene dibromide contained yet styrene dibromide. The characteristic feature of the reaction was that a phenolic substance, styrene dibromide, and carbon dioxide were produced. The formation of the phenolic substance may be accompanied by the production of formaldehyde and carbon dioxide. Detailed investigation of the reaction mechanism of styrene with hydrogen bromide and oxygen will be made in future.

Summary

(1) The reaction of diphenylethylene, atropic acid, and styrene with the mixture of hydrogen bromide and oxygen were studied. In the case of diphenylethylene, diphenylbromomethane, ω-bromoacetophenone, diphenylethylene dibromide, phenol and carbon dioxide were obtained as reaction products. A reaction mechanism was proposed to explain how these compounds were produced.

(2) In the case of atropic acid, a large amount of α-hydroxy-β-bromohydratopic acid and a small amount of ω,ω-dibromoacetophenone and of carbon dioxide were obtained. A consideration on the mechanism of the formation of these products was given on the basis of the identified products and their semiquantitative estimation.

(3) Addition of hydrogen bromide to atropic was carried out under various conditions. No reversal of the direction of addition of hydrogen bromide was observed contrary to the previous reference.

(4) The reaction of styrene with the mixture of hydrogen bromide and oxygen added an example yielding a phenolic substance in the reaction.

Tne author wishes to express his hearty thanks to Prof. Y. Urushibara and Prof. O. Simamura for their kind guidance and encouragement throughout this work. The author is indebted to Dr. S. Tanaka for the infrared spectra measurement and their interpretation.

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Studies on Antibiotics and Related Substances. III. Oxazolidines Derived from Some α-Hydroxy Schiff Bases and a Synthesis of DL-*threo*-*1-p-Nitrophenyl-2-amino-1,3-propanediol**

By Tetsuo SUAMI and Sumio UMEZAWA

(Received June 28, 1956)

The present authors[1] previously reported that the reduction of *threo*-β-phenylserine[2] ethyl ester[3–6] by Raney nickel catalyst resulted in the formation of a new compound $C_{13}H_{17}NO_2$ (I), m. p. 138–139°C, which gave an N-acetyl oxazolidine derivative (II), m. p. 148–148.5°C, on acetylation with acetic anhydride at room temperature. II was led to DL-*threo*-1-*p*-nitrophenyl-2-amino-1,3-propanediol by a synthetic route.

The present paper describes further investigations on the constitutions of I and II and also the synthesis of DL-chloramphenicol[7] from II in details.

The failure of II to hydrolyze under Kunz's conditions[8] demonstrated that II was an N-acetyl derivative. Consequently, the authors had assumed I to be an oxazolidine derivative. To establish the differentiation between oxazolidines and isomeric Schiff bases, the infrared and ultraviolet spectra of I and II

* Presented in part before the Division of Organic Chemistry at the Annual Meeting of the Chemical Society of Japan, Tokyo, April 2, 1955. Previous papers: This Bulletin, 27, 477 (1954); 29, 417 (1956).

1) S. Umezawa and T. Suami, This Bulletin, 27, 477 (1954).

2) E. Erlenmeyer, Jr., *Ber.*, 25, 3445 (1892).

3) G. Carrara and G. Weitnauer, *Gazz. chim. ital.*, 79, 856 (1949).

4) E. D. Bergmann, H. Bendas and W. Taub, *J. Chem. Soc.*, 1951, 2673.

5) G. W. Moersch, U. S., 2,538,792 (1951).

6) K. N. F. Shaw and S. W. Fox, *J. Am. Chem. Soc.*, 75, 3420 (1953).

7) J. Controulis, M. C. Rebstock and H. M. Crooks, Jr., *J. Am. Chem. Soc.*, 71, 2463 (1949).

8) A. Kunz aud C. S. Hudson, *J. Am. Chem. Soc.*, 48, 1982 (1926).

were measured. Infrared spectrum of I (Fig. 1) showed the presence of C=N bond in 1642 cm^{-1}, while II (acetylated product) showed no band in the absorption region of the C=N double bond and showed the triplet at 1089, 1168 and 1212 cm^{-1}, very likely because of the O—C—N system in the expected oxazolidine system[4], was found.

For the corresponding *p*-nitro derivatives (III and IV) of I and II, the infrared spectra were studied (Fig. 1). As was expected, DL-*threo*-1-*p*-nitrophenyl-2-benzylideneamino-1, 3-propanediol (III) prepared by the condensation of DL-*threo*-1-*p*-nitrophenyl-2-amino-1, 3-propanediol with benzaldehyde showed the presence of C=N bond in 1631 cm^{-1}, while the acetylated product (IV) of III showed no band in the absorption region of the C=N bond and showed the triplet at 1099, 1172 and 1217 cm^{-1} [4].

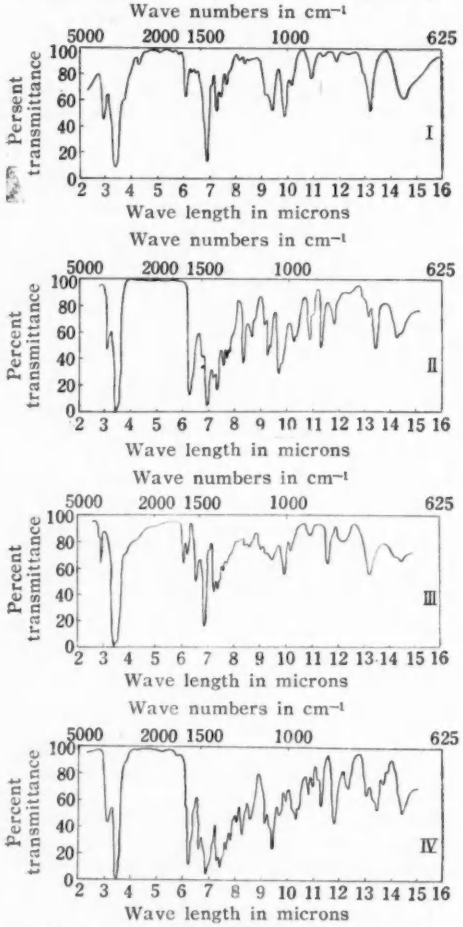

Wave numbers in cm⁻¹
5000 2000 1500 1000 625
Percent transmittance
100 80 60 40 20 0
I
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wave length in microns
Wave numbers in cm⁻¹
5000 2000 1500 1000 625
Percent transmittance
100 80 60 40 20 0
II
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wave length in microns
Wave numbers in cm⁻¹
5000 2000 1500 1000 625
Percent transmittance
100 80 60 40 20 0
III
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wave length in microns
Wave numbers in cm⁻¹
5000 2000 1500 1000 625
Percent transmittance
100 80 60 40 20 0
IV
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wave length in microns

Fig. 1. Infrared absorption spectra of Schiff bases and corresponding oxazolicine compounds (in Nujol).
I) DL-*threo*-1-Phenyl-2-benzylideneamino-1, 3-propanediol.
II) DL-*threo*-N-Acetyl-2-phenyl-4-(α-hydroxybenzyl)oxazolidine.
III) DL-*threo*-1-*p*-Nitrophenyl-2-benzylideneamino-1, 3-propanediol.
IV) DL-*threo*-N-Acetyl-2-phenyl-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine.

In addition, the ultraviolet absorption spectra of I, II, III and IV were measured. As the ultraviolet absorption spectra of the Schiff base of ethyl *p*-nitrophenylserinate and its acetylated product had been reported by Bergmann et al.[9], DL-*threo*-1-phenyl-2-amino-1, 3-propanediol and DL-*threo*-1-*p*-nitrophenyl-2-amino-1, 3-propanediol were condensed with *p*-nitrobenzaldehyde to give the Schiff bases (I′, III′) respectively which were further acetylated with acetic anhydride to give N-acetyl oxazolidine derivatives (II′, IV′).

Absorption maxima of these derivatives are recorded in Table I. The melting points, analyses and yields are given in Tables II and III.

DL-*threo*-1-*p*-Nitrophenyl-2-(*p*-nitrobenzylidene)amino-1, 3-propanediol (III′) possessed an absorption maximum (λ 2680 Å, log ε 4.29) similar to that reported for the Schiff base of ethyl *p*-nitrophenylserinate (λ 2700 Å, log ε 4.39)[9]. Correspondingly, the acetylated product (IV′) of III′ possessed a maximum (λ 2670 Å, log ε 4.34) similar to that of the acetylated product of the Schiff base of ethyl *p*-nitrophenylserinate (λ 2655 Å, log ε 4.35)[9].

Acetylated product of the Schiff base obtained from DL-*threo*-1-phenyl-2-amino-1, 3-propanediol and benzaldehyde showed three maxima (2520, 2580 and 2640 Å).

The condensation products of DL-*threo*-1-phenyl-2-amino-1, 3-propanediol and DL-*threo*-1-*p*-nitrophenyl-2-amino-1, 3-propanediol with *o*-nitro and *m*-nitrobenzaldehyde were further prepared and then acetylated to give oxazolidine derivatives, which failed to hydrolyze under Kunz's conditions[8]. The melting points, analyses and yields of these products are given in Table II and III.

Two isomeric structures—one with the oxazolidine ring containing the oxygen of the primary alcohol and the other with the oxazolidine ring containing the oxygen of the secondary alcohol—were expected for the acetylated product II which was prepared from the Schiff base I.

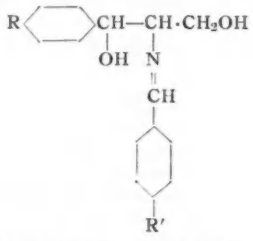
Considering the fact that II was not further acetylated on standing with acetic anhydride for three hours at room tempera-

9) E. D. Bergmann, H. Bendas and Ch. Resnick, *J. Chem. Soc.*, 1953, 2564.

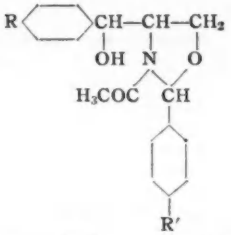
TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF SCHIFF BASES AND N-ACETYL OXAZOLIDINE DERIVATIVES

Derivatives	Wave Lengths and Intensities of Maxima (in Chloroform)	
	$\lambda_{max.}$ (Å)	$\log \varepsilon_{max.}$
I	2510	3.59
II	2580	2.68
III***	2760	4.14
IV	2680	4.30
I'**	2660	4.16
II'*	—	—
III'	2680	4.29
IV'	2670	4.34



I R=H, R'=H
III R=NO_2, R'=H
I' R=H, R'=NO_2
III' R=NO_2, R'=NO_2



II R=H, R'=H
IV R=NO_2, R'=H
II' R=H, R'=NO_2
IV' R=NO_2, R'=NO_2

* This derivative did not crystallize.

** This derivative was reported recently by S. Umezawa et al.[10]

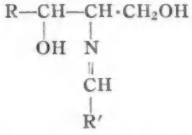
*** This derivative was reported by Iliceto et al.[11]

ture, while DL-*threo*-1-phenyl-2-amino-1, 3-propanediol was acetylated by acetic anhydride in half an hour at room temperature to yield DL-*threo*-1-phenyl-2-acetamido-3-acetoxy-1-propanol[12], II was considered to be of the former structure combined with the oxygen of the primary alcohol.

Recently, two analogous cases were reported. McCasland et al.[13] demonstrated that the condensation product of 2-amino-cyclohexanol and benzaldehyde had the structure

TABLE II

CONDENSATION PRODUCTS OF AMINOALCOHOLS AND ALDEHYDES (SCHIFF BASES)



R	R'	Formula	M. p., °C	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl	Phenyl	$C_{15}H_{17}NO_2$	138–139	78.6	—	—	—	—	—	—
Phenyl	*o*-Nitrophenyl	$C_{15}H_{14}N_2O_4$	122–123	50.1	—	—	—	—	9.33	9.17
Phenyl	*m*-Nitrophenyl	$C_{15}H_{14}N_2O_4$	98–99	11.1	—	—	—	—	9.33	9.45
p-Nitrophenyl	Phenyl	$C_{15}H_{16}N_2O_4$	158–159*	77.5	63.99	64.24	5.37	5.33	—	—
p-Nitrophenyl	*o*-Nitrophenyl	$C_{15}H_{15}N_3O_6$	140–141**	55.3	—	—	—	—	12.17	11.97
p-Nitrophenyl	*m*-Nitrophenyl	$C_{15}H_{15}N_3O_6$	135–136.5	49.2	—	—	—	—	12.17	12.52
p-Nitrophenyl	*p*-Nitrophenyl	$C_{15}H_{15}N_3O_6$	173–174	55.3	—	—	—	—	12.17	12.32

* M. p. reported by Iliceto et al.[11] was 155–156°C.

** M. p. reported by Iliceto et al.[11] was 144–146°C.

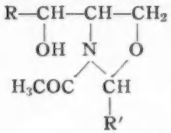
10) T. Suami, I. Uchida and S. Umezawa, This Bulletin, **29**, 417 (195).

11) A. Iliceto and E. Scoffone, *Gazz. chim. ital.*, **81**, 133 (1951).

12) L. M. Long and H. D. Troutman, *J. Am. Chem. Soc.*, **71**, 2469 (1949).

13) G. E. McCasland and E. C. Horswill, *J. Am. Chem. Soc.*, **73**, 3923 (1951).

TABLE III
ACETYLATION PRODUCTS OF SCHIFF BASES (OXAZOLIDINE DERIVATIVES)



R	R′	Formula	M. p., °C	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl	Phenyl	$C_{18}H_{19}NO_3$	148–148.5	42.9	72.70	72.97	6.44	6.49	4.71	4.64
p-Nitrophenyl	Phenyl	$C_{18}H_{18}N_2O_5$	178–180	35.1	63.15	63.25	5.30	5.31	—	—
p-Nitrophenyl	*o*-Nitrophenyl	$C_{18}H_{17}N_3O_7$	242–244	53.5	—	—	—	—	10.85	10.98
p-Nitrophenyl	*m*-Nitrophenyl	$C_{18}H_{17}N_3O_7$	202–203.5	53.5	—	—	—	—	10.85	10.40
p-Nitrophenyl	*p*-Nitrophenyl	$C_{18}H_{17}N_3O_7$	170–171	62.4	—	—	—	—	10.85	11.12

of a Schiff base, while its N-benzoyl derivative had that of oxazolidine. As mentioned above, Bergmann et al.[9] also described that the condensation products of the *threo* and *erythro*-forms of *p*-nitrophenylserine ethyl ester with *p*-nitrobenzaldehyde had the structures of Schiff bases and acetylation converted them into diastereoisomeric oxazolidines.

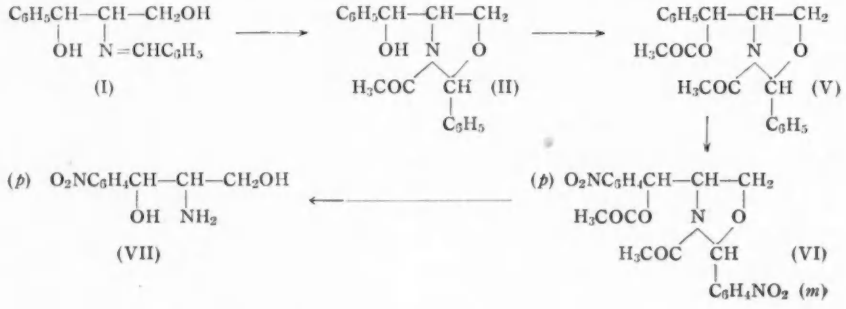
It is of interest to extend the observation that the acetylation of the Schiff bases of *β*-phenylserinol and its derivatives converted them into oxazolidine compounds.

Schiff base I was easily hydrolyzed on warming with 0.95N hydrochloric acid at 60°C for one hour, to give DL-*threo*-1-phenyl-2-amino-1, 3-propanediol and benzaldehyde.

It is interesting that the rate of catalytic reduction of the C=N bond in Schiff base I was very slow and practically stopped after the reduction of the ester group. In this regard, Goldberg and Nace[14] reported recently on the selected reduction of the unsaturated Schiff base system C=C—C=N.

Starting from the above described DL-*threo*-N-acetyl-2-phenyl-4-(*α*-hydroxybenzyl) oxazolidine II, DL-chloramphenicol[7], an important antibiotic found by scientists of Parke, Davis and Company, was synthesized through the route described below. Further acetylation of II with acetic anhydride in pyridine gave a viscous product (V), which, on nitration with mixed acid under dry ice-cooling for thirty minutes and then ice-cooling for thirty minutes, and finally at 15°C for thirty minutes, gave a viscous product containing a small amount of crystals. The latter, after recrystallization, appeared to be the diacetyl derivative of 2-(*m*-nitrophenyl)-4-(*α*-hydroxy-*p*-nitrobenzyl)oxazolidine (VI), m. p. 192–193°C. The diacetyl derivative gave one mole of acetic acid on hydrolysis under Kunz's conditions[8], demonstrating that VI is an N, O-diacetyl oxazolidine compound. VI gave *m*-nitrobenzaldehyde on refluxing with 4.5 N hydrochloric acid.

The crude, viscous-oily, nitration product containing VI mainly, was refluxed with 3 N hydrochloric acid for three hours and the reaction solution was concentrated by evaporation under reduced pressure, followed by pH adjustment with 5 N sodium hydroxide



14) E. P. Goldberg and H. R. Nace, *J. Am. Chem. Soc.*, 77, 359 (1955).

to 10, to give DL-*threo*-1-*p*-nitrophenyl-2-amino-1, 3-propanediol (VII) melting at 143.5–145°C, which did not depress the melting point of an authentic sample obtained by the synthetic route from *p*-nitroacetophenone[15].

VII was acylated with dichloroacetamide to yield DL-chloramphenicol.

Experimental

Reduction of DL-*threo*-Phenylserine Ethyl Ester with Raney Nickel Catalyst.—DL-*threo*-1-Phenyl-2-benzylideneamino-1, 3-propanediol (I).—Ten grams of DL-*threo*-phenylserine ethyl ester[3-6] was dissolved in 50 cc. of absolute ethanol and reduced in an autoclave for six hours, at 50–60°C under 110 atms. H_2 with 17 g. of Raney nickel W-1[16]. After standing overnight, the catalyst was filtered off and the solvent was removed under reduced pressure to yield a pale yellow oily residue. After it was settled in a desiccator overnight, colorless crystals appeared in it. The crystals were collected and washed with ether to yield 2.5 g. (41.0%) of colorless crystals. They were recrystallized twice from ethanol. Colorless plates, m. p. 138–139°C.

Anal. Found: C, 75.26; H, 6.74; N, 5.53. Calcd. for $C_{18}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%.

Infrared (Fig. 1) and ultraviolet absorption spectra (Table I) were measured.

2.0 g. of I was hydrolyzed for one hour with 10 cc. of 0.95 N hydrochloric acid at 60°C. Benzaldehyde which separated on the solution was extracted with ether, and the aqueous layer was concentrated at 40°C under reduced pressure. The residue was redissolved in 5 cc. of cold water. After an excess of potassium carbonate was added to the solution, it was extracted five times with ethyl acetate. The combined ethyl acetate solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield 1.0 g. (76.4%) of a pale yellow oil. This oil crystallized on standing at room temperature with two drops of ethyl acetate. The crystals were recrystallized twice from ethyl acetate. Yield, 0.59 g. (45.1%). Colorless crystals, m. p. 87–88°C. They did not depress the melting point of an authentic sample of DL-*threo*-1-phenyl-2-amino-1, 3-propanediol obtained by the method of Controulis et al.[7].

Acetylation of DL-*threo*-1-Phenyl-2-benzylideneamino-1, 3-propanediol.—DL-*threo*-N-Acetyl-2-phenyl-4-(α-hydroxybenzyl) oxazolidine (II).—2.0g. of DL-*threo*-1-phenyl-2-benzylideneamino-1, 3-propanediol (I) was added to 4.0 cc. of acetic anhydride with agitation at room temperature. The colorless crystals which appeared immediately were collected and washed with ether to yield 1.9 g. of the crude product melting at 145–146°C (81.5%). This was recrystallized twice from methanol to yield 1.0 g. (42.9%) of colorless crystals melting at 148–148.5°C. This product was not further acetylated on standing with ten volumes of acetic anhydride for three hours at room temperature. This failed to hydrolyze under Kunz's conditions[8].

Anal. Found: C, 72.97; H, 6.49; N, 4.64. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71%.

Infrared (Fig. 1) and ultraviolet absorption spectra (Table I) were measured.

Condensation of DL-*threo*-1-Phenyl-2-amino-1, 3-propanediol and DL-*threo*-1-*p*-Nitrophenyl-2-amino-1, 3-propanediol with Benzaldehyde, *o*-, *m*- and *p*-Nitrobenzaldehyde.—DL-*threo*-1-Phenyl-2-benzylideneamino-1, 3-propanediol (I) and other Schiff bases were all prepared by essentially the same procedure.

DL-*threo*-1-Phenyl-2-benzylideneamino-1, 3-propanediol (I).—1.0 g. of DL-*threo*-1-phenyl-2-amino-1, 3-propanediol was added to a mixture of 0.7 g. of freshly distilled benzaldehyde and a small quantity of ethyl acetate. After the mixture was stirred at room temperature for fifteen minutes, ethyl acetate was removed in vacuo. The residual solid was washed with ether to obtain 1.5 g. (98.2%) of a colorless powder melting at 133–135°C.

It was recrystallized twice from ethanol. Yield, 1.2 g. (78.6%). Colorless crystals, m. p. 138–139°. They did not depress the melting point of the sample of I obtained by the reduction of DL-*threo*-phenylserine ethy ester with Raney nickel catalyst.

DL-*threo*-1-Phenyl-2-(*o*-nitrobenzylidene) amino-1, 3-propanediol was purified by recrystallization from acetone, DL-*threo*-1-*p*-nitrophenyl-2-(*m*-nitrobenzylidene) amino-1, 3-propanediol and DL-*threo*-1-*p*-nitrophenyl-2-(*p*-nitrobenzylidene)amino-1, 3-propanediol were purified by recrystallization from methanol, whereas, DL-*threo*-1-phenyl-2-(*m*-nitrobenzylidene)amino-1, 3-propanediol was not purified. The melting points, analyses and yields are given in Table II.

Acetylation of the Above Described Schiff Bases.—Acetylation products of DL-*threo*-1-phenyl-2-(*o*-nitrobenzylidene)amino-1, 3-propanediol and DL-*threo*-1-phenyl-2-(*p*-nitrobenzylidene)amino-1, 3-propanediol[10] failed to crystallize. The following four products were obtained as crystals.

Acetylated products (oxazolidine derivatives) were all prepared by essentially the same procedure as that of DL-*threo*-N-acetyl-2-phenyl-4-(α-hydroxybenzyl)oxazolidine (II), but DL-*threo*-N-acetyl-2-phenyl-4-(α-hydroxy-*p*-nitrobenzyl) oxazolidine was prepared by the following procedure.

DL-*threo*-N-Acetyl-2-phenyl-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine (IV).—0.5 g. of III was added to 2.0 cc. of acetic anhydride. After standing at room temperature for two hours, the reaction solution was diluted with water, neutralized with sodium bicarbonate, and extracted with ethyl acetate. The ethyl acetate solution was dried over anhydrous sodium sulfate, and evaporated under reduced pressure to yield 0.5 g. of a pale yellow oily residue. It was dissolved in a small quantity of ether and added to an equal volume of petroleum ether. After standing overnight in a refrigerator, 0.3 g. (52.6%) of colorless crystals were obtained and recrystallized from acetone. Yield, 0.2 g. (35.1%). Colorless crystals, m. p. 178–180°C.

Anal. Found: C, 63.25; H, 5.31. Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30%.

This failed to hydrolyze under Kunz's condi-

15) L. M. Long and H. D. Troutman, *J. Am. Chem. Soc.*, 71, 2473 (1949).

16) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, 68, 1471 (1946).

tions[8]). Infrared (Fig. 1) and ultraviolet absorption spectra (Table I) were measured.

DL-*threo*-N-Acetyl-2-(*o*-nitrophenyl)-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine and DL-*threo*-N-acetyl-2-(*m*-nitrophenyl)-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine were purified by recrystallization from acetone. DL-*threo*-N-Acetyl-2-(*p*-nitrophenyl)-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine (IV') was purified by recrystallization from acetone-petroleum ether. The melting points, analyses and yields are given in Table III.

Synthesis of DL-Chloramphenicol from II.—DL-*threo*-N, O-Diacetyl-2-phenyl-4-(α-hydroxybenzyl) oxazolidine (V).—5.5 g. of II was dissolved in 14.0 cc. of dry pyridine and 8.0 cc. of acetic anhydride. After standing at room temperature for forty-eight hours, the solution was poured into ice water. The mixture was extracted with ethyl acetate and the ethyl acetate solution was washed with 0.5N hydrochloric acid, 1% sodium carbonate solution, and water. Then the ethyl acetate solution was concentrated in vacuo and 6.4 g. of a yellow viscous oil was obtained.

DL-*threo*-N, O-Diacetyl-2-(*m*-nitrophenyl)-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine (VI).—6.4 g. of V was added to 30 cc. of a 1:1 mixture of nitric acid (d. 1.38) and sulfuric acid (d. 1.84) with dry ice cooling and vigorous shaking. After thirty minutes, the reaction flask was transferred to an ice bath for thirty minutes, and then kept at room temperature for thirty minutes. The solution was quenched on 200 g. of ice and immediately neutralized with sodium bicarbonate. The product was extracted five times with ethyl acetate and the combined ethyl acetate solution was washed with cold water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield 8.0 g. (98.8%) of a pale yellow viscous product. The crude product was added to absolute acetone to yield 0.97 g. (12.0%) of colorless crystals melting at 192–193°C.

Anal. Found: C, 55.45; H, 4.24; N, 9.44; O-acetyl, 11.0. Calcd. for $C_{20}H_{19}N_3O_8$: C, 55.94; H, 4.46; N, 9.79; O-acetyl 10.0%.

This product gave one mole of acetic acid on hydrolysis under Kunz's conditions[8]).

0.5 g. of these crystals were refluxed for four hours with 18 cc. of 4.5 N hydrochloric acid and then settled at room temperature overnight. Pale yellow needles melting at 56–57°C appeared in the solution and they did not depress the melting point of an authentic sample of *m*-nitrobenzaldehyde.

The solution remaining after the Kunz's determination for O-acetyl was evaporated under reduced pressure to remove acetone. The colorless crystals which precipitated in the solution were collected and washed with water. The crystals melted at 201–203°C and did not depress the melting point of DL-*threo*-N-acetyl-2-(*m*-nitrophenyl)-4-(α-hydroxy-*p*-nitrobenzyl)oxazolidine.

DL-*threo*-1-*p*-Nitrophenyl-2-amino-1, 3-propanediol (VII).—7.2 g. of crude VI was refluxed for three hours with 80 cc. of 3 N hydrochloric acid. The solution was washed with ether to remove an oily precipitate of nitrobenzaldehyde and concentrated under reduced pressure. The residue was dissolved in 5 cc. of cold water and the pH of the solution was adjusted to 10 with 5 N sodium hydroxide with ice cooling. After standing overnight in a refrigerator, 1.75 g. (49.2%) of the crude base melting at 129–133°C was obtained. The base was repeatedly recrystallized from hot water to yield pale yellow crystals melting at 143.5–145°C which did not depress the melting point of an authentic sample obtained by the method of Long et al.[15])

DL-*threo*-1-*p*-Nitrophenyl-2-dichloroacetamido-1, 3-propanediol.—2.0 g. of VII was finely mixed with 1.2 g. of dichloroacetamide, and the mixture was heated on a boiling water bath for three hours, and dissolved in ethyl acetate. The solution was filtered, washed with 0.5 N hydrochloric acid to remove the unreacted free base and then with water, dried over anhydrous sodium sulfate, passed through a short chromatographic column of 10 g. alumina to remove the coloring matter and then evaporated under reduced pressure to yield 2.3 g. of a crystalline residue melting at 128–137°C. It was recrystallized from ethylene dichloride and washed with ether. Pale yellow crystals, m.p. 147–149°C. Yield, 1.2 g. (39.1%). The product was further recrystallized from ethyl acetate-petroleum ether to yield colorless crystals melting at 149–150°C, which did not depress the melting point of an authentic sample obtained by the method of Long et al.[15])

One mg. of these crystals was equivalent to 512 γ of natural chloramphenicol[17]) by the cup assay method (test organism E.coli).

Summary

1) When Erlenmeyer's β-phenylserine ethyl ester was reduced with Raney nickel catalyst, DL-*threo*-1-phenyl-2-benzylideneamino-1, 3-propanediol (a Schiff base) was obtained as a main product. The structure was demonstrated by means of its infrared and ultraviolet absorption spectra.

2) It was found that DL-*threo*-1-phenyl-2-benzylideneamino-1, 3-propanediol gave DL-*threo*-N-acetyl-2-phenyl-4-(α-hydroxybenzyl) oxazolidine on acetylation with acetic anhydride.

3) The condensation products of DL-*threo*-1-phenyl-2-amino-1, 3-propanediol and DL-*threo*-1-*p*-nitrophenyl-2-amino-1, 3-propanediol with benzaldehyde, *o*-, *m*- and *p*-nitrobenzaldehyde were prepared and acetylated to give corresponding oxazolidine derivatives, which failed to hydrolyze under Kunz's conditions. Infrared and ultraviolet absorption spectra of some of these compounds were observed. Acetylated derivatives failed to show the characteristic absorption of $\rangle C{=}N-$ bond in the 1660–1610 cm^{-1} region.

17) J. Ehrlich, Q. R. Bartz, R. M. Smith and D. A. Joslyn, *Science*, **108**, 417 (1947).

4) DL-Chloramphenicol was synthesized from DL-*threo*-N-acetyl-2-phenyl-4-(α-hydroxybenzyl)oxazolidine.

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Constituents of the Mucilage of Gloiopeltis Furcata

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Certain species of the *Gloiopeltis* family of *Rhodophyceae* contain a water-soluble mucilage, which on dissolution in water forms a highly viscous solution. It is widely used in this country as a sizing agent for silk textiles and as a thickening agent for mortar and plaster. The mucilage is a metallic salt of the sulfate ester of a polysaccharide, which on acid hydrolysis produces chiefly D-galactose together with a small amount of L-arabinose and L-fucose[1,2]. But there has also been reported the presence of a considerable amount of an unidentified constituent showing a Seliwanoff's ketose reaction[1,2]. On the other hand, it is established that agar-agar contains 3,6-anhydro-L-galactose as well as D-galactose as the chief constituent[3], and that carrageenin contains an enanthiomorph of the anhydrosugar present in agar in addition to D-galactose[4,5]. Both agar and carrageenin also contain a small amount of L-galactose[5,6]. Since 3,6-anhydro-galactose shows a distinct Seliwanoff's reaction, it is most probable that the unidentified constituent of the *Gloiopeltis* mucilage is 3,6-anhydro-galactose. This has been proved to be the case as reported herein, and the anhydro-sugar has been shown to be of the L-series. In addition, the presence of a small amount of L-galactose has also been confirmed.

The mucilage used in this study was extracted from commercial "sheet Funori", which is prepared from *Gloiopeltis furcata* by conglutinating the plant bodies with each other by means of their own mucilage. The mucilage extracted has a specific rotation, $[\alpha]_D^{15} = -20.6°$, in water and contains 18.5% of sulfate. It was then subjected to complete methanolysis. After an appropriate treatment the methanolysate was separated by column chromatography into 3,6-anhydro-L-galactose dimethylacetal and a mixture of methyl D- and L-galactoside. The former product was hydrolysed to give a reducing sugar, which was then identified as its phenylosazone. The latter mixture was further separated into crystalline methyl α-D-galactoside and a residual syrup, which on hydrolysis gave rise to a mixture of D- and L-galactose. Then D-galactose was removed therefrom as much as possible by crystallization, and the residue was treated with ethylmercaptan and concentrated hydrochloric acid. L-Galactose was isolated in the form of crystalline DL-galactose diethylmercaptal, which was further identified as its penta-acetate. The yields of the products have indicated that the *Gloiopeltis* mucilage used contains 3,6-anhydro-L-galactose, D-galactose and L-galactose in the approximate ratio of 8:12:1.

Experimental

Evaporation and concentration were carried out under reduced pressure below 40°. Specific rotations were measured in aqueous solutions unless otherwise stated. The melting points are uncorrected.

Material.—Twenty grams of commercial sheet of *Gloiopeltis furcata* was extracted with water (2 l.) in a boiling water bath for two hours. After filtration through a bed of Celite-active carbon, the extract was concentrated and precipitated with 95% ethanol. The product, collected and pressed in a cotton sack, was dehydrated with absolute ethanol and then ether, air-dried and finally ground to powder; yield 6.5 g. (moisture 9.33%); $[\alpha]_D^{15} = -20.6°$ (*c* 0.63); found: ash, 13.14%; SO_4 total, 18.48%; SO_4 in ash, 6.84%, of the mucilage, respectively, on the moisture-free basis.

1) K. Kawakami, *J. Soc. Chem. Ind. Japan*, **13**, 341 (1910).
2) E. Takahashi, *J. Coll. Agr. Hokkaido Imp. Univ.*, **8**, 183 (1920).
3) f. i. see C. Araki, This Bulletin, **29**, 543 (1956).
4) C. Araki and S. Hirase, ibid, **29**, 991 (1956); A. N. O'Neil, *J. Am. Chem. Soc.*, **77**, 2837, 6324 (1955).
5) E. E. Percival, *Chemistry & Industry*, **1954**, 1487.
6) C. Araki and K. Arai, Collection of Treatises in Commemoration of 45th Anniversary of Kyoto Technical College, p. 80 (1948).

Methanolysis.—The mucilage (1.50 g., moisture 9.33%) in 3% methanolic hydrogen chloride (20 cc.) was heated under reflux for twenty-five hours. The resulting solution was neutralized with silver carbonate, filtered and concentrated to a syrup, which was then treated with 0.3N-barium hydroxide solution (20 cc.) at 60° for two hours. Excess barium hydroxide was removed by neutralization with carbon dioxide and filtration, and the filtrate was concentrated to a syrup. It was dissolved in water and deionized by passing the solution through columns of Amberlite IR-120 and IR-4B resins in succession, the resins being subsequently washed with water. The effluent and washings were combined and concentrated to a syrup; yield 0.779 g. (57.3% of the mucilage); $[\alpha]_D^{24}=+46.9°$ (*c* 0.64). Paper chromatographic examination, using *n*-butanol-ethanol-water (4:1:2 by volume) as a solvent and *o*-aminophenol reagent[7] as a spraying reagent, indicated the presence of 3,6-anhydro-galactose dimethylacetal (R_f 0.67[8]).

Chromatographic Separation.—The deionized methanolysate (0.754 g.) obtained above was chromatographed on a column (2.5×30 cm.) of powdered filter paper, *n*-butanol-water (6:1) being used as a developer until the effluent showed no longer a spot of 3,6-anhydro-galactose dimethylacetal on a paper chromatogram. Then the column was developed with 80% aqueous methanol (300 cc.). Butanolic and methanolic effluents were separately evaporated to dryness, giving 3,6-anhydro-L-galactose dimethylacetal and a mixture of methyl D- and L-galactoside, respectively, in yields of 0.290 g. and 0.456 g. Since L-galactose amounts to 7.9% of total galactose as described later, 3,6-anhydro-L-galactose, D-galactose and L-galactose are in the molar ratio 7.6:11.6:1.

3,6-Anhydro-L-galactose Dimethylacetal.—3,6-Anhydro-L-galactose dimethylacetal above obtained was a colorless syrup, which was further purified by dissolution in dry acetone followed by filtration and subsequent evaporation; $[\alpha]_D^{27}=-25.9°$ (*c* 0.80); OCH_3, found: 27.73% (calcd. for $C_8H_{16}O_5$: 29.81%). It showed a distinct Seliwanoff's ketose reaction.

3,6-Anhydro-L-galactose.—The above dimethylacetal (0.3 g.) was hydrolysed with 0.02N-sulfuric acid (10 cc.) in a boiling water bath for two hours. The solution was neutralized with barium carbonate, filtered and concentrated to dryness, when 3,6-anhydro-L-galactose was obtained as a syrup (0.2 g.). It reduced a Fehling's solution at room temperature.

Phenylosazone: The sugar above obtained was converted to its phenylosazone by reaction with phenylhydrazine in the presence of dilute acetic acid in the usual manner. The osazone was twice recrystallized from ethanol-water (2:1), forming yellow needles; m.p. 217°; $[\alpha]_D^{30}=-65.9°$ (an initial value, pyridine-methanol (2:3), *c* 0.44) → −52.3° (an equilibrium value). Reported values[9] are m.p. 217° and $[\alpha]_D=-52.8°$ (an equilibrium value, pyridine-methanol). Admixture with an authentic sample showed no depression of the melting point.

Methyl α-D-Galactoside.—When the mixture of methyl D- and L-galactoside, obtained from the methanolic effluent of chromatography, was dissolved in ethanol and kept in a refrigerator, methyl α-D-galactoside was deposited as its monohydrate; yield 0.191 g. It was recrystallized from ethanol, giving prisms; m.p. 94–98°, not depressed on admixture with an authentic sample; $[\alpha]_D^{32}=+175°$ (*c* 1.00); OCH_3, found: 14.63% (calcd. for $C_7H_{14}O_6 \cdot H_2O$: 14.61%).

D-Galactose.—The mother liquor, separated from crystals of methyl α-D-galactoside monohydrate, was concentrated to a syrup (0.262 g.), which was then subjected to hydrolysis with N-sulfuric acid (5 cc.) in a boiling water bath for four hours. The product (0.239 g.), isolated in the usual manner, was crystallized from methanol, affording D-galactose; yield 0.107 g. The recrystallized sample melted at 164–165° and had a specific rotation $[\alpha]_D^{27}=+80.8°$ (an equilibrium value, *c* 0.73). Mixed melting point determination showed no depression.

DL-Galactose Diethylmercaptal.—The mother liquor, separated from crystals of D-galactose, was concentrated to a syrup (0.123 g.), which was then combined with two other batches. The resulting mixture was extracted with boiling absolute ethanol. On cooling the extract gave crystals (0.10 g.) melting at 140–144° and having a specific rotation, $[\alpha]_D^{28}=+32.5°$ (an equilibrium value, *c* 0.80). The value of the specific rotation indicates that the crystals are a mixture of D-galactose and L-galactose, the former predominating. The filtered mother liquor was concentrated to a syrup (0.20 g.), $[\alpha]_D^{27}=+4.6°$ (an equilibrium value, *c* 0.65). It showed on a paper chromatogram a single spot corresponding to galactose. This observation and the low value of a specific rotation may show that the above-mentioned syrup is nearly pure DL-galactose. Then, on being calculated for a single batch, the yield (0.067 g.) of DL-galactose amounts to 15.8% of the whole galactose, and hence that of L-galactose is 7.9%.

For conclusive identification, the syrupy DL-galactose above obtained was converted to its diethylmercaptal as follows. The syrup (0.20 g.) was dissolved in concentrated hydrochloric acid (*d* = 1.20, 2 cc.), and ethylmercaptan (2 cc.) was added. After being vigorously shaken for fifteen minutes under ice-cooling, the reaction mixture was diluted with ice-water, immediately neutralized with excess lead carbonate, filtered and concentrated to dryness. The residue was extracted with boiling acetone. On evaporation the extract afforded DL-galactose diethylmercaptal melting at 121-124°; yield 0.18 g. A pure compound was obtained on recrystallization from acetone; m.p. 126-127°; $[\alpha]_D^{28}=\pm 0°$ (*c* 0.80); SC_2H_5[10], found: 42.80% (calcd. for

7) S. Hirase, C. Araki and S. Nakanishi, This Bulletin, **26**, 183 (1953).
8) C. Araki and S. Hirase, ibid., **27**, 109 (1954).
9) C. Araki, *J. Chem. Soc. Japan*, **65**, 725 (1944).
10) S. Hirase and C. Araki, This Bulletin, **28**, 481 (1955).

$C_{10}H_{22}O_5S_2$: 42.68%). The values previously reported by two of the present authors[11] are m.p. 126-127° and $[\alpha]_D = \pm 0°$. The admixture of an authentic sample showed no depression of the melting point.

For further identification, the diethylmercaptal was converted to its penta-acetate by acetylation with acetic anhydride and pyridine. The acetate obtained was recrystallized from aqueous methanol; m.p. 112–113°; $[\alpha]_D^{18} = \pm 0°$ (chloroform, *c* 0.75). Reported values are m.p. 112–113° and $[\alpha]_D = \pm 0°$ (chloroform). Admixture with an authentic sample showed no depression of the melting point.

Summary

1. The mucilage of *Gloiopeltis furcata* has been investigated by the complete methanolysis method.

2. 3,6-Anhydro-L-galactose dimethylacetal and methyl D-galactoside have been isolated from the methanolysate. In addition, L-galactose has also been isolated in the form of the crystalline DL-galactose diethylmercaptal.

3. The yields of the isolates have indicated that the mucilage used contains 3,6-anhydro-L-galactose, D-galactose and L-galactose in the approximate molar ratio of 8 : 12 : 1.

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11) C. Araki and S. Hirase, This Bulletin,, **26**, 463 (1953).

Studies on Antibiotics and Related Substances. IV. Synthesis of* DL-*threo*-β-*Cyclohexylserine and* DL-*threo*-2-*Dichloroacetamido*-1-*cyclohexylpropane*-1,3-*diol*

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Synthesis of DL-*threo*-β-cyclohexylserine and its Derivatives.— In earlier papers[1] the reduction of E. Erlenmeyer's phenylserine[2] with Raney nickel catalyst in ethanol was found to yield DL-*threo*-2-benzylideneamino-1-phenylpropane-1,3-diol (a Schiff base) as the main product. The present paper records the result of the reduction of the N-acetyl ester of phenylserine.

When ethyl DL-*threo*-N-acetyl-β-phenylserinate (I) was reduced with hydrogen over Raney nickel catalyst in ethanol, the product was ethyl DL-*threo*-N-acetyl-β-cyclohexylserinate (II) melting at 94–95°C. Hydrolysis of the N-acetyl derivative (II) by refluxing in dilute hydrochloric acid was followed by concentration of the solution *in vacuo* and subsequent neutralization to pH 6.8 with sodium hydroxide yielding crystalline DL-β-cyclohexylserine (III) melting at 231°C (dec.).

Confirmation of the structure of β-cyclohexylserine (III) was obtained in the following ways. III was oxidized by sodium periodate to give 62% crude yield of cyclohexanealdehyde, which was identified as the 2,4-dinitrophenylhydrazone and did not depress the melting point of an authentic sample of 2,4-dinitrophenylhydrazone of cyclohexanealdehyde prepared by hydrolysis and decarboxylation of ethyl cyclohexylglycidate[3]. The N-acetylcyclohexylserinate(II) was further acetylated with acetic anhydride in the presence of pyridine to yield ethyl N,O-diacetyl-β-cyclohexylserinate, m.p. 115.5–116.5°C, which, on hydrolysis under Kunz's conditions[4] (for O-acyl group), liberated two moles of carboxylic acid. As anticipated, ethyl N-acetylcyclohexylserinate liberated one mole of carboxylic acid under the same conditions. Thus, the presence of the cyclohexyl group and that of contiguous hydroxyl and amino groups in β-cyclohexylserine (III) were ascertained.

Since it is well established that the configuration of Erlenmeyer's phenylserine, the starting material, is of the *threo* configuration, it is necessary for III to be DL-*threo*-β-cyclohexylserine.

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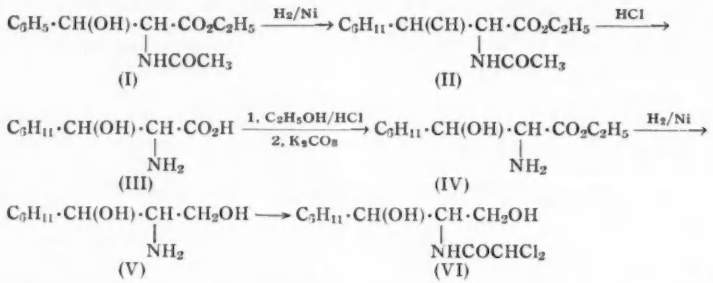
1) S. Umezawa and T. Suami, This Bulletin, **27**, 477 (1954); T. Suami, and S. Umezawa, ibid., **29**, 979 (1956).

2) E. Erlenmeyer, *Ber.*, **25**, 3445 (1892).

3) G. Darzens, *Compt. rend.*, **142**, 214 (1906).

4) A. Kunz and C. S. Hudson, *J. Am. Chem. Soc.*, **48**, 1982 (1926); M. L. Wolfrom, M. Königsberg and S. Stolzberg, ibid., **58**, 409 (1936).



Synthesis of DL-*threo*-2-Dichloroacetamido-1-cyclohexylpropane-1, 3-diol.—The derivatives of 2-aminopropane-1, 3-diol have received considerable attention in recent years as analogues of chloramphenicol, an important antibiotic found by scientists of Parke, Davis and Company[5]. Ashley and Davis[6] recently synthesized an isomer of 2-amino-1-cyclohexylpropane-1, 3-diol by reduction of 2-nitro-1-cyclohexylpropane-1, 3-diol which was obtained by condensation of cyclohexanealdehyde with β-nitroethanol in the presence of sodium methoxide. The dichloroacetyl derivative of this isomer of 2-amino-1-cyclohexylpropane-1, 3-diol had no antibacterial activity and it was likely that this isomer is of the *erythro* configuration.

It became of interest to us to convert the ethyl ester of the above-mentioned β-cyclohexylserine (III) into the corresponding aminoalcohol. Ethyl DL-*threo*-β-cyclohexylserinate (IV), m. p. 60–61°C, was readily prepared from the above-mentioned β-cyclohexylserine (III) by the Fischer-Speier method. The catalytic reduction* of IV with hydrogen over Raney nickel catalyst at 150 kg./cm² and 100°C for 4.5 hours gave DL-*threo*-2-amino-1-cyclohexylpropane-1, 3-diol(V), m.p. 112–113°C. Acylation of V by refluxing with methyl dichloroacetate gave DL-*threo*-2-dichloroacetamido-1-cyclohexylpropane-1, 3-diol (VI), m. p. 167–168°C. It has now been found that, though the chloramphenicol analogue possesses the *threo* configuration, it shows no significant antibacterial activity.

Experimental

Ethyl DL-*threo*-N-Acetyl-β-phenylserinate(I).—Ethyl DL-*threo*-phenylserinate was prepared by treatment of Erlenmeyer's phenylserine in absolute ethanol with dry hydrogen chloride followed by liberating the aminoester by rendering alkaline with potassium carbonate, as reported by G. Carrara and G. Weitnauer[7]. The compound was very hygroscopic and decomposed upon prolonged standing.

With the aid of gentle warming, 6.0 g. of ethyl DL-*threo*-β-phenylserinate was dissolved in 6 cc. of glacial acetic acid and 2.8 cc. of acetic anhydride was added with stirring. The ethyl DL-*threo*-N-acetyl-β-phenylserinate separated as a crystalline mass and was filtered after keeping for thirty minutes, and then washed well with ether and water. The yield was 6.8 g. (91.8%) and m. p. 175–176°C. The compound was almost insoluble in ether and acetone, soluble in hot ethyl acetate and ethanol. Recrystallization from ethanol failed to raise the melting point.

Anal. Found: N, 5.52. Calcd. for $C_{13}H_{17}O_4N$: N, 5.57%.

Ethyl DL-*threo*-N-Acetyl-β-cyclohexylserinate (II).—A solution of 6.0 g. of ethyl DL-*threo*-N-acetyl-β-phenylserinate (I) in 150 cc. of absolute ethanol was shaken with 10 g. of Raney nickel catalyst[8] at 50–60°C and 130 kg./cm² for sixteen hours. The content was filtered to remove the catalyst and the solvent was removed *in vacuo*. The oily residue was dissolved in 25 cc. of ether and the solution was diluted with an equal volume of petroleumether, whereupon there separated a crystalline precipitate, which was collected after standing overnight; yield 5.3 g. (86.8%) and m. p. 83–88°C. Two recrystallizations from ether afforded 1.5 g. of pure ethyl DL-*threo*-N-acetyl-β-cyclohexylserinate (II) melting at 94–95°C. The compound liberated one mole of carboxylic acid on hydrolysis under Kunz's conditions[4].

Anal. Found: C, 60.96; H, 8.81; N, 5.65; saponification equivalent*, 275. Calcd. for $C_{13}H_{23}O_4N$: C, 60.68; H, 8.95; N, 5.44%; saponification equivalent*, 257.

DL-*threo*-β-Cyclohexylserine (III).—A mixture of 0.8 g. of ethyl DL-*threo*-N-acetyl-β-cyclohexylserinate in 16 cc. of 5% hydrochloric acid was refluxed for 2.5 hr. The solution was evaporated *in vacuo* to dryness and the resulting solid was dissolved in 10 cc. of water and the solution was neutralized to pH 6.8 by addition of 5 N sodium hydroxide. After standing overnight the cry-

5) J. Ehrlich, Q. R. Bartz, R. M. Smith and A. A. Joslyn, *Science*, **106**, 417 (1947); J. Controulis, M. C. Rebstock and H. M. Crooks, Jr., *J. Am. Chem. Soc.*, **71**, 2463 (1949), and later papers.

6) N. J. Ashley and M. Davis, *J. Chem. Soc.*, **1952**, 63.

* When this reduction was carried out at 50°C and 150 kg./cm² for seven hours, the original aminoester was recovered in a high yield.

7) G. Carrara and G. Weitnauer, *Gazz. chim. ital.*, **79**, 856 (1949); *C. A.* **44**, 7268 (1650).

8) Organic Syntheses, **21**, 15 (1940).

* Saponified under Kunz's conditions.

stalline precipitate was separated from the solution; yield 0.42 g. (72.5%) and m. p. 223°C (dec.) Two recrystallizations from distilled water gave 0.22 g. of pure DL-*threo*-β-cyclohexylserine, m. p. 231°C (dec.).

Anal. Found: C, 57.50; H, 9.38; N, 7.18. Calcd. for $C_9H_{17}O_3N$: C, 57.73; H, 9.15; N, 7.48%.

Ethyl DL-*threo*-N, O-Diacetyl-β-cyclohexylserinate.—A mixture of 0.52 g. of ethyl DL-*threo*-N-acetyl-β-cyclohexylserinate (II), 3.0 cc. of acetic anhydride and 2 cc. of pyridine was allowed to stand overnight at room temperature. The solution was poured into about 20 cc. of ice water with stirring. After standing for 2.5 hr., a yield of 0.40 g. of crude ethyl DL-*threo*-N, O-diacetyl-β-cyclohexylserinate was collected, m. p. 113.5–114.5°C. Purification for analysis was accomplished by dissolving the product in ether with subsequent addition of petroleum ether; yield 0.16 g. and m. p. 115.5–116.5°C. The N, O-diacetyl ester liberated two moles of carboxylic acid on hydrolysis under Kunz's conditions[4], indicating the presence of an O-acetyl and a carbethoxyl group.

Anal. Found: C, 60.13; H, 8.19; N, 4.96; O-acetyl, 13.8%. Calcd. for $C_{15}H_{25}O_5N$: C, 60.18; H, 8.35; N, 4.68; O-acetyl, 14.4%.

Periodate Oxidation of DL-*threo*-β-Cyclohexylserine.—A solution of 0.65 g. of sodium periodate hydrate in 25 cc. of distilled water containing ten drops of 6 N sulfuric acid was added with stirring to a solution of 0.5 g. of DL-*threo*-β-cyclohexylserine (III) in 15 cc. of distilled water containing five drops of 6 N sulfuric acid and warmed to about 40°C. After about thirty minutes the solution gave off the characteristic smell of an aldehyde. After standing overnight the reaction mixture was extracted four times with 15 cc. of ether. The pale-yellow ethereal extract was washed in turn with 5 cc. of 1% sodium carbonate solution and 5 cc. of distilled water and dried with anhydrous sodium sulfate. Removal of ether afforded 0.18 g. (62%) of crude hexahydrobenzaldehyde.

The crude hexahydrobenzaldehyde was dissolved in 1 cc. of ethanol and distilled water was added until the solution became just turbid. Again, ethanol was added until the mixture just clarified. To the solution were added 0.2 g. of semicarbazide hydrochloride and 0.3 g. of sodium acetate. The mixture was warmed for several minutes and allowed to stand overnight at room temperature. Concentration *in vacuo* gave 0.12 g. (44%) of crude semicarbazone, m. p. 168.5–170°C. After two recrystallizations from distilled water pure hexahydrobenzaldehyde semicarbazone, m. p. 172–173°C, was obtained, undepressed on admixture with the authentic sample prepared by decarboxylation of cyclohexylglycidic acid, as described below.

To a solution of 4.0 g. of sodium hydroxide in 11.5 cc. of distilled water was added 9.5 g. of ethyl cyclohexylglycidate[3] and the mixture was stirred for 6.5 hr. at 45–50°C. After standing overnight the reaction mixture was acidified with 6 N hydrochloric acid using Congo Red as indicator and then steamdistilled for about 4.5 hr. Extraction with benzene followed by vacuum distillation gave 10 g. of hexahydrobenzaldehyde, b. p. 56°C/24 mm. The semicarbazone melted at 171–172°C after recrystallization from distilled water.

Ethyl DL-*threo*-β-Cyclohexylserinate (IV).—A solution of 6.3 g. of DL-*threo*-β-cyclohexylserine (III) in 65 cc. of absolute ethanol was saturated with dry hydrogen chloride and allowed to stand overnight. Concentration *in vacuo* left an oily product, which was dissolved in 35 cc. of distilled water, washed twice with 10 cc. of ethyl acetate and rendered alkaline by addition of solid potassium carbonate. Extraction with ethyl acetate followed by removal of the solvent *in vacuo* gave 6.37 g. (86.5%) of crude ethyl DL-*threo*-β-cyclohexylserinate which could not be crystallized on prolonged standing. The crude ester was used in subsequent reduction without further purification.

However, it was found that the aminoester forms a crystalline oxalate and this furnishes a method of purifing and crystallizing the aminoester.

A sample of 0.4 g. of the crystalline oxalate prepared as described below was dissolved in 8 cc. of distilled water and rendered alkaline to pH 10 with potassium carbonate and extracted five times with 8 cc. of ethyl acetate, which were combined and dried with anhydrous sodium sulfate. Removal of the solvent *in vacuo* left a syrup which crystallized after standing overnight; yield 0.31 g. and m. p. 47–52°C. Four recrystallizations from petroleumether gave 0.09 g. of pure ethyl DL-*threo*-β-cyclohexylserinate, m. p. 60–61°C.

Anal. Found: N, 6.55. Calcd. for $C_{11}H_{21}O_3N$: N, 6.51%.

Oxalate of IV.—A solution of 0.11 g. of oxalic acid hydrate in 1 cc. of absolute ethanol was added to a solution of 0.15 g. of the crude syrup of ethyl DL-*threo*-β-cyclohexylserinate (IV) in 0.5 cc. of absolute ethanol. After addition of ether followed by stirring, the mixture was allowed to stand for two hours at room temperature. Colorless minute crystals which separated, were collected and washed with ether; yield 0.12 g. and m. p. 182–185°C (dec.). Recrystallizations from ethanol-water mixture (7:3) gave the oxalate of ethyl DL-*threo*-β-cyclohexylserinate (IV), $C_6H_{11}\cdot{}_1CH(OH)\cdot CHNH_2\cdot CO_2C_2H_5\cdot 1/2(COOH)_2$, m. p. 181–181.5°C (dec.).

Anal. Found: N, 5.57. Calcd. for $C_{12}H_{23}O_5N$: N, 5.38%.

DL-*threo*-2-Amino-1-cyclohexylpropane-1, 3-diol (V).—A solution of 2.83 g. of ethyl DL-*threo*-β-cyclohexylserinate (a crude syrup) in 50 cc. of absolute ethanol was hydrogenated over 4 g. of Raney nickel catalyst[8] at 95–100°C for 4.5 hr. under an initial pressure of 130 kg./cm². The catalyst was removed by filtration. The filtrate was concentrated *in vacuo* to about a fifth of its bulk, filtered from a small amount of solid impurity and the filtrate was again concentrated to give 2.97 g. of an oily product, which deposited a crystalline solid on standing overnight. Three recrystallizations from ethyl acetate gave colorless needles of DL-*threo*-2-amino-1-cyclohexylpropane-1, 3-diol; yield 0.32 g. (12.3%) and m. p. 112–113°C.

Anal. Found: C, 62.40; H, 10.89; N, 7.87. Calcd. for $C_9H_{19}O_2N$: C, 62.39; H, 11.05; N, 8.09%.

DL-*threo*-2-Dichloroacetamido-1-cyclohexylpropane-1,3-diol (VI).—A mixture of 0.13 g. of DL-

threo-2-amino-1-cyclohexylpropane-1, 3-diol (V) and 1.5 cc. of methyl dichloroacetate was refluxed for two hours. Removal of excess of the ester left 0.08 g. of a pale-green syrup. Washing with petroleum-ether and addition of ethyl acetate gave 0.03 g. (14%) of DL-*threo*-2-dichloroacetamido-1-cyclohexylpropane-1, 3-diol, m. p. 167–168°.

Anal. Found: N, 4.54. Calcd. for $C_{11}H_{19}O_3NCl_2$: N, 4.92%C.

The chloramphenicol analogue showed no significant antibacterial activity (test organism E. coli).

Summary

(1) When the N-acetyl ethyl ester of Erlenmeyer's phenylserine was reduced with hydrogen over Raney nickel catalyst, ethyl DL-*threo*-N-acetyl-β-cyclohexylserinate was obtained in crude yields as high as 86.8 %. Subsequent hydrolysis with dilute hydrochloric acid afforded DL-*threo*-β-cyclohexylserine, which gave hexahydrobenzaldehyde by periodate oxidation.

(2) Raney nickel reduction of ethyl DL-*threo*-β-cyclohexyl-serinate afforded DL-*threo*-2-amino-1-cyclohexylpropane-1, 3-diol. The aminoalcohol was converted into DL-*threo*-2-dichloroacetamido-1-cyclohexylpropane-1, 3-diol, a chloramphenicol analogue.

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*Studies on Azeotropic Mixtures. I. General Considerations**

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Introduction

In 1900 Zawidzki[1] showed in his pioneering study on the liquid solutions that non-ideal binary solutions could be classified into two types with positive and negative deviations from Raoult's law. He also showed that when the two components of such solution had sufficiently equal vapor pressures, the positive type yielded a maximum point and the negative one a minimum point in the vapor pressure-composition curve. These points are called azeotropic points and the solutions are said, at such points, to form azeotropes or azeotropic mixtures. It is well known that the liquid phase of an azeotrope may be transformed to the vapor phase without changing the composition of any of these phases. This is a condition of practical importance, since it limits the possibility of separation by fractional distillation.

Recently Prigogine[2] has investigated azeotropic phenomenon assuming the solution to be regular. In this paper we will treat the same phenomenon along his line but from a more explicit standpoint of molecular interaction, with the aim of comparing the azeotrope-forming power of a number of solutions.

Our assumption is that an azeotropic mixture can be regarded as a strictly regular solution[3] near its boiling point, which can be treated with the quasi-crystalline model, introducing explicit representation for interaction energy of component molecules. Component molecules of the azeotropic mixture are usually more or less polar or non-spherically shaped and at a lower temperature they are prevented by their dipoles or shapes from executing free rotation. Thus it is by no means a good approximation to assume that they constitute a strictly regular solution, i. e., solution with spherical molecules of sufficiently equal size and of weak interaction energy. However, near its boiling point, the rotations of component molecules will become free enough to allow them to be regarded as constituting a strictly regular solution. Thus, near the boiling point, though all molecules distributed on each site of the quasi-crystalline lattice may not be always executing completely free rotation, their dipole or other figure axes are considered to orient at random.

The above assumption seems to be too crude to interpret the azeotropic phenomenon quantitatively, but some successes obtained in this paper suggest that we are not far from the right way. It may be mentioned that we have some suggestions[4] to interpret

* Presented at the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956.

1) J. V. Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

2) I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans (1954), chapt. XXVIII.

3) E. A. Guggenheim, "Mixture", Oxford (1952), chapt. IV.

4) R. S. Halford, *J. Chem. Phys.*, **8**, 496 (1940); K. S. Pitzer, *J. Chem. Phys.*, **7**, 583 (1939).

the deviation from Trouton's or Hildebrand's constant of real pure liquids by similar assumptions.

Derivation of Basic Formula for an Azeotropic Mixture

In the following study we will restrict our consideration to the binary solution. The molar Helmholtz free energy of pure components 1 and 2 is

$$\Delta_m F = RT(x_1 \ln x_1 + x_2 \ln x_2) + N x_1 x_2 w. \quad (1)$$

Here, x_i is the mole fraction of component $i(i=1,2)$, T the absolute temperature, N the Avogadro number and R the gas constant. The equation is the zeroth approximation (treatment of random mixing) of the quasi-chemical treatment of strictly regular solution developed by Guggenheim[3] and it will be shown later that the approximation is quite reasonable within the range considered, so that we do not need further higher terms. w is a quantity determining the non-ideality of the solution and is called molecular interchange energy. We will give its explicit form in terms of the absolute average potential energy ε of the pair of molecules:

$$w = \frac{z}{2}(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}). \quad (2)$$

z denotes the average number of nearest neighbors of a given molecule, i.e., the coordination number of the molecule on the quasi-lattice. In making a single exchange of molecule between liquid 1 and 2, we destory z 1-1 and z 2-2 pairs and form $2z$ 1-2 pairs of nearest neighbors, and the increase of potential energy is $2w$.

Denoting μ_i and γ_i the chemical potential and the activity coefficient of the ith component and the superscript o referring to the pure component, we obtain the chemical potentials from equation (1) by a usual procedure,

$$\mu_1 - \mu_1^0 = RT \ln x_1 + N x_2^2 w, \quad (3)$$

$$\mu_2 - \mu_2^0 = RT \ln x_2 + N x_1^2 w. \quad (4)$$

Further from the definition of the activity coefficient, we have

$$\mu_1 - \mu_1^0 = RT \ln x_1 \gamma_1, \quad (5)$$

$$\mu_2 - \mu_2^0 = RT \ln x_2 \gamma_2. \quad (6)$$

From these equations, we get

$$\ln \gamma_1 = \frac{Nw}{RT} x_2^2, \quad (7)$$

$$\ln \gamma_2 = \frac{Nw}{RT} x_1^2. \quad (8)$$

These are Hildebrand's relations for the regular solution and Nw corresponds to his constant B[5].

We will now turn to the equilibrium between the vapor and the liquid phase of binary azeotropic mixture[6]. In equilibrium state the chemical potentials of component i in both phases are equal:

$$\mu_i = \mu_{i'},$$

where

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i, \quad (9)$$

$$\mu_{i'} = \mu_i^{0'} + RT \ln x_{i'} \gamma_{i'}. \quad (10)$$

In these equations a single prime refers to the vapor phase and no prime to the liquid one. Thus we obtain

$$\ln \frac{x_{i'}\gamma_{i'}}{x_i \gamma_i} = -\frac{\mu_i^{0'} - \mu_i^0}{RT}. \quad (11)$$

As the activity coefficient is the function of temperature and pressure, we obtain the following equation by considering an infinitesimal increment of the chemical potential in going from the liquid to the vapor phase,

$$\delta\left(\ln \frac{x_{i'}\gamma_{i'}}{x_i \gamma_i}\right) = \left\{\frac{\partial\left(-\frac{\mu_i^{0'} - \mu_i^0}{RT}\right)}{\partial T}\right\}_p dT + \left\{\frac{\partial\left(-\frac{\mu_i^{0'} - \mu_i^0}{RT}\right)}{\partial p}\right\}_T dp = \frac{\Delta_v H_i^0}{RT^2} dT - \frac{\Delta_v V_i^0}{RT} dp, \quad (12)$$

since

$$\left\{\frac{\partial(\mu_i/T)}{\partial T}\right\}_p = -\frac{H_i}{T^2} \quad (13)$$

and

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = V_i. \quad (14)$$

Here, $\Delta_v H_i^0$ is the molar heat of vaporization and $\Delta_v V_i^0$ the molar volume change of vaporization of ith pure component. We integrate the equation from an initial state T_i^0, p_i^0, $x_i^0 = 1$, $x_i^{0'} = 1$, $\gamma_i^0 = 1$, $\gamma_i^{0'} = 1$, corresponding to the vapor-liquid equilibrium of the pure component i, to a final equilibrium state (azeotropic point) T^a, p^a, x_i, $x_{i'}$, γ_i, $\gamma_{i'}$, so that

$$\ln \frac{x_{i'}\gamma_{i'}}{x_i \gamma_i} = \int_{T_i^0}^{T^a} \frac{\Delta_v H_i^0}{RT^2} dT - \frac{1}{RT} \int_{p_i^0}^{p^a} \Delta_v V_i^0 dp. \quad (15)$$

5) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes", Reinhold (1950), 121.
6) I. Prigogine and R. Defay, op. cit., chapt. XVIII.

An azeotrope is formed when, in a closed system, the mass of one of the phases increases at the expense of the others without changing the composition. When the equilibrium is attained from, the definition of azeotrope formation, we have a condition as follows:

$$x_i = x_{i'}. \tag{16}$$

At a constant pressure (1 atm.) we have to consider only the first term of the right hand of equation (15). For most practical cases, it is sufficiently accurate to assume the heat of vaporization to be independent of temperature in the range considered and the vapor to be perfact ($\gamma_{i'}=1$), so we have

$$\ln \gamma_i = \frac{\Delta_v H_i^0}{RT_i^0}\frac{T_i^0 - T^a}{T^a} = \frac{\Delta_v S_i^0}{R}\frac{T_i^0 - T^a}{T^a}, \tag{17}$$

where $\Delta_v S_i^0$ is the molar entropy of vaporization of ith pure component. At a constant temperature T^a, we have, again taking the vapor to be perfect and neglecting the liquid volume compared with vapor one ($\Delta_v V_i^0 = V_i^{0'} - V_i^0 \simeq V_i^{0'} \simeq RT^a/p$),

$$\gamma_i = p^a/p_i^0. \tag{18}$$

Thus we can combine equations (17) and (18) with (7) and (8) at the azeotropic point to obtain final equations for the azeotropic mixture.

At constant pressure (p=1 atm.) we have

$$\Delta_v S_1^0(T_1^0 - T^a) = Nwx_2^2, \tag{19}$$

and

$$\Delta_v S_2^0(T_2^0 - T^a) = Nwx_1^2. \tag{20}$$

At constant temperature T^a we have

$$RT^a \ln (p^a/p_1^0) = Nwx_2^2, \tag{21}$$

and

$$RT^a \ln (p^a/p_2^0) = Nwx_1^2. \tag{22}$$

Entirely the same equations as those from (19) to (22) can be derived from the final equations given by Prigogine[7] except that he has not retained Nw (α in his equations) in an explicit form (2) in his further discussion of azeotropic mixtures. In the following discussion we will mainly use the equations (19) and (20), since most of the azeotropic data are investigated under constant pressure (1 atm.).

Here, it should be mentioned that if we take higher terms in the quasi-chemical treatment, we have, instead of equations (19) and (20),

$$\Delta_v S_1^0(T_1^0 - T^a) = Nwx_2^2\left\{1 + \frac{2x_1(x_1-x_2)}{2!}\left(\frac{2w}{zkT^a}\right) + \frac{2x_1(x_1-x_2)(1-6x_2+6x_2^2)}{3!}\left(\frac{2w}{zkT^a}\right)^2 + \cdots\right\} \tag{23}$$

and

$$\Delta_v S_2^0(T_2^0 - T^a) = Nwx_1^2\left\{1 - \frac{2x_2(x_1-x_2)}{2!}\left(\frac{2w}{zkT^a}\right) - \frac{2x_2(x_1-x_2)(1-6x_2+6x_2^2)}{3!}\left(\frac{2w}{zkT^a}\right)^2 - \cdots\right\}, \tag{24}$$

where k is Boltzmann's constant.

In the quasi-chemical approximation[8] w/kT cannot for example, exceed 2.301 for a body-centered cubic lattice, z=8, or 2.188 for a face-centered cubic lattice, z=12, without phase separation. Thus within the range $1 > x_2 \geq \frac{1}{2}$ in (23) and the range $1 > x_1 \geq \frac{1}{2}$ in (24), even the second term of the series cannot exceed 0.072 or 0.046 for the respective lattice, the higher terms being much smaller. Therefore, as far as we take the data from these ranges or their vicinity it will be sufficiently accurate to leave only the first terms as we did, but as x_2 approaches 0 in (23) and x_1 approaches 0 in (24) the error of the above approximation will be considerable. As the first step, however, we will start with the approximate equations (19) and (20) to compare the azeotrope-forming power of a number of azeotropic mixtures.

Azeotrope-forming Power and Condition for Azeotrope Formation

It is of interest for our purpose to see whether an azeotrope is of a maximum or minimum type according to the sign of w, and how the magnitude of w determines the range of boiling points or vapor pressures of pure components allowable in azeotrope formation.

If w is positive in sign we have the minimum azeotrope with $T_1^0, T_2^0 > T^a$ from equations (19) and (20) or positive azeotrope with $p^a > p_1^0, p_2^0$ from equation (21) and (22). If w is negative we have the maximum azeotrope with $T_1^0, T_2^0 < T^a$ or negative azeotrope with $p^a < p_1^0, p_2^0$ conversely.

For an azeotrope to have existence in homogeneous solution, x_i must lie between 0 and 1. Therefore as conditions of azeotrope existence we can readily derive from equations (19) and (20) or (21) and (22),

$$-\frac{Nw}{\Delta_v S_2^0} \leq T_1^0 - T_2^0 \leq \frac{Nw}{\Delta_v S_1^0} \tag{25}$$

7) I. Prigogine and R. Defay op. cit., p. 455 (28.25), (28.22).

8) E. A. Guggenheim, op. cit., p. 41.

or $$-\frac{Nw}{RT^a} \leq \ln (P_1^0/P_2^0) \leq \frac{Nw}{RT^a} \quad (26)$$

respectively.

Equation (26) is also derived by Prigogine[9]. The equality in equation (25) will give maximum and minimum boiling temperatures of pure component 1. Between these temperatures various kinds of component 1 are allowed to form azeotropes with a fixed component 2. Thus w is considered as a measure of the azeotropeforming power of solutions. The larger the value of w, the more different boiling points the component 1 and 2 can have in azeotrope formation.

Discussion

For the discussion of various kinds of azeotropic mixtures it is appropriate to group them into four classes* as shown in Tables I–IV, according to the following different types of intermolecular forces: (1) force between non-polar molecules (dispersion effect): (2) force between permanent dipoles (dipole-dipole interaction): (3) force between a permanent dipole and an induced dipole (dipole-induced dipole interaction). For simplicity, we will involve in the type (2) the attraction due to hydrogen bonding that is essentially electrostatic. Among these types the second appears to have the most important effect on azeotrope formation.

(a) Dispersion Force Solutions

London[10] derived for the absolute value of an attractive potential between 1 and 2 molecule

$$\epsilon_{12} = -\frac{3\alpha_1\alpha_2}{2r_{12}^6}\frac{h\nu_{01}\cdot h\nu_{02}}{h\nu_{01}+h\nu_{02}}, \quad (27)$$

where h is Planck's constant, α_i the polarizability of the ith molecule and $h\nu_{0i}$ is the energy closely related to the ionization potential of the i-th molecule. In the model under consideration the distances between all molecules may be taken as nearly equal:

$$r_{11}=r_{12}=r_{22}=r.$$

Equations (2) and (27) can now be used to obtain

$$w=\frac{3}{2}\frac{z}{2}\frac{h}{r^3}\left\{\frac{\nu_{01}\alpha_1^2}{2}+\frac{\nu_{02}\alpha_2^2}{2}-2\frac{\nu_{01}\cdot\nu_{02}}{\nu_{01}+\nu_{02}}\alpha_1\alpha_2\right\}.$$

Noting that

$$\frac{\nu_{01}\cdot\nu_{02}}{\nu_{01}+\nu_{02}} \leq \frac{\sqrt{\nu_{01}\cdot\nu_{02}}}{2},$$

we conclude that

$$w \geq \frac{3}{2}\frac{z}{2}\frac{h}{r^3}\left\{\frac{\nu_{01}\alpha_1^2}{2}+\frac{\nu_{02}\alpha_2^2}{2}-\sqrt{\nu_{01}\cdot\nu_{02}}\,\alpha_1\alpha_2\right\}. \quad (28)$$

Thus we see that if the interactions are caused solely by dispersion force we must always have

$$w \geq 0$$

and so azeotropes, if any, are always minimum. Examples are found in azeotropes between two different types of hydrocarbons, i.e. aromatics-paraffins and aromatics-naphthens. Another examples are azeotropes between non-polar liquids and paraffinic or naphthenic hydrocarbons. Some of them (No. 1 to 5 for the former, 6 for the latter examples) are listed in Table I together with their calculated w values. Here we see that values of w calculated from equation (19) or (20) show agreement as a whole.

(b) Solutions Involving Addition Compounds

We shall have an "addition compound" in a case where the potential energies ϵ_{11} and ϵ_{22} are of the same order of magnitude, while,

$$\epsilon_{12} \gg \epsilon_{11},\ \epsilon_{22},$$

and so

$$w < 0.$$

We thus have maximum type azeotropes in this case. It appears reasonable to attribute these intermolecular forces mainly to the dipole interaction due to hydrogen bonding between components 1 and 2, but here we will not proceed further to the quantitative discussion as in the case of free molecules because of the inapplicability of simple Boltzmann's statistics. A number of instances are found in azeotropes between polyhalogen compounds and the compounds involving donor atoms such as esters, ketones, aldehydes, ethers and acetals. Examples are listed in Table II.

(c) Solutions Involving Associations in Non-polar Solvents

In this class ϵ_{22} is far more important than ϵ_{11} and ϵ_{12}, where ϵ_{22} is considered to be due mainly to dipole-dipole, ϵ_{11} to dispersion effect and ϵ_{12} to dipole-induced dipole interactions. The ϵ_{22} is frequently due to strong hydrogen bonding. That is,

$$\epsilon_{22} \gg \epsilon_{12} > \epsilon_{11}$$

and so

$$w > 0.$$

We thus have minimum type azeotropes. Examples are listed in Table III.

(d) Solutions Involving Associations in Polar Solvents

In a way similar to class (c) ϵ_{22} is greater

9) I. Prigogine and R. Defay, op. cit., p. 465 (28.50).

* Similar classification was given by I. Prigogine and R. Defay, op. cit., p. 385ff.

10) F. London, *Trans. Faraday Soc.*, **33**, 19 (1937), *J. Phys. Chem.*, **46**, 305 (1942).

than ε_{12} or ε_{11}, but the differences between them are not so great as in class (c), the difference between ε_{11} and ε_{12} being smaller than that between ε_{22} and ε_{12}:

$$\varepsilon_{22}>\varepsilon_{12},\ \varepsilon_{22}>\varepsilon_{11},\ (\varepsilon_{22}-\varepsilon_{12})>\ \varepsilon_{11}-\varepsilon_{12}\ ,$$

so still we have

$$w>0.$$

Here all ε's are considered to be due to a certain extent to dipole interaction (or hydrogen bonding). Thus azeotropes are minimum, but their extents are not so great as in the class (c), with a few exceptions. Examples are given in Table IV.

TABLE I

AZEOTROPIC DATA OF CLASS (a)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2[a] (mole fraction)	$\Delta_v S_1^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	$\Delta_v S_2^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Benzene	2,2-Dimethylpentane	80.15	79.1	75.85	0.526	(20.3)	20.8	0.24	0.40
2	Benzene	2,4-Dimethylpentane	80.15	80.8	76.7	0.536	(20.3)	20.8	0.40	0.48
3	Benzene	Cyclohexane	80.15	80.6	77.7	0.537	20.4	20.8	0.20	0.24
4	Toluene	2,3,4-Trimethylpentane	110.7	113.5	109.5	0.615	(20.3)	20.8	0.19	0.20
5	Toluene	*cis-trans-cis*-1,2,4-trimethylcyclopentene	110.7	109.3	107.4	0.439	(20.3)	20.8	0.24	0.24
6	Carbon disulfide	Cyclopentane	46.25	49.4	44.0	0.652	(20.3)	20.0	0.25	0.37

Azeotropic data are taken from Horsely's "Azeotropic Data" published in 1956 by the American Chemical Society except for butanethiol (R.L. Denyer, F.A. Fidler and R.A. Lowry, *Ind. Eng Chem.*, **41**, 2727 (1949).

a) Mole fractions calculated from wt. % in Horsely's data.

b) Values taken from "International Critical Table", Vol. V (1929).

Values enclosed in parentheses are those presumed from similar substances.

TABLE II

AZEOTROPIC DATA OF CLASS (b)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2[a] (mole fraction)	$\Delta_v S_1^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	$\Delta_v S_2^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Trichloromethane	2-Propanone	61.2	56.10	64.43	0.640	22.0	21.0	−0.45	−0.52
2	Bromodichloromethane	2-Butanone	90.2	79.6	90.85	0.790	21.7	(21.0)	−0.39	−0.31
3	Bromodichloromethane	3-Methyl-2-butanone	90.2	95.4	97.2	0.348	(21.0)	(21.0)	−0.31	−0.35
4	Bromodichloromethane	Propyl Ethanonate	90.2	101.6	102.3	0.207	21.9	(21.0)	−0.36	−0.40
5	Bromodichloromethane	Methyl Carbonate	90.2	90.35	91.95	0.499	21.8	(21.0)	−0.14	−0.15
6	Trichloroethylene	Diethoxymethane	86.9	87.9	89.2	0.477	(21.7)	21.0	−0.12	−0.18

TABLE III

AZEOTROPIC DATA OF CLASS (c)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2[a] (mole fraction)	$\Delta_v S_1^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	$\Delta_v S_2^{0}$[b] $\left(\frac{\text{cal}}{M°C}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Trichloromethane	2,3-Dimethylbutane	61.2	58.0	55.5	0.391	(20.3)	21.0	0.33	0.32
2	Acetonitrile	Carbon tetrachloride	81.6	76.75	75.3	0.434	20.4	20.2	1.26	1.04
3	Acetonitrile	Benzene	81.6	80.1	73	0.494	20.8	20.2	0.61	0.68
4	Nitromethane	Toluene	101.2	110.75	96.5	0.648	20.8	22.1	0.71	0.84

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2[a] (mole fraction)	$\Delta_v S_1^{0b}$ $\left(\frac{\text{cal}}{M°C}\right)$	$\Delta_v S_1^{0b}$ $\left(\frac{\text{cal}}{M°C}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
5	Nitromethane	Cyclohexane	101.2	80.75	70.2	0.349	20.4	22.1	1.76	1.62
6	Nitromethane	Heptane	101.2	98.4	80.2	0.492	20.6	22.1	1.55	1.79
7	Butanethiol	Heptane	98.58	98.40	95.45	0.520	20.6	(23.4)	0.23	0.32
8	Butanethiol	Methylcyclohexane	98.58	101.05	97.0	0.603	20.2	(23.4)	0.22	0.23
9	Phenol	Indene	182.2	183.0	177.8	0.523	(20.3)	(22)	0.39	0.43
10	1,2-Benzenediol	2-Methylnaphthalene	245.9	241.15	233.25	0.431	(20.3)	(22.5)	0.86	0.88
11	1,3-Benzenediol	2-Methylnaphthalene	281.4	241.15	240.05	0.131	(20.3)	(23.5)	1.30	1.29

TABLE IV
AZEOTROPIC DATA OF CLASS (d)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2[a] (mole fraction)	$\Delta_v S_1^{0b}$ $\left(\frac{\text{cal}}{M°C}\right)$	$\Delta_v S_2^{0b}$ $\left(\frac{\text{cal}}{M°C}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Acetonitrile	Methyl Propanoate	81.6	79.85	76.2	0.479	21.9	20.2	0.35	0.40
2	Acetonitrile	Propyl methanoate	81.6	80.85	76.5	0.513	22.0	20.2	0.36	0.44
3	Acetonitrile	1-Chlorobutane	81.6	78.5	67.2	0.526	(20.7)	20.2	0.85	1.29
4	Acetonitrile	1-Chloro-2-methylpropane	81.6	68.85	62.0	0.360	(20.7)	20.2	1.09	0.97
5	Nitromethane	1-Bromobutane	101.2	101.5	90.0	0.691	(20.7)	22.1	0.50	2.60
6	Nitromethane	1-Bromo-2-methylpropane	101.2	91.4	84.0	0.536	(20.7)	22.1	0.53	1.77
7	Nitromethane	2-Iodopropane	101.2	89.45	82.0	0.579	(20.7)	22.1	0.46	2.40
8	Nitromethane	2-Pentanone	101.2	102.35	99.15	0.643	(21)	22.1	0.16	0.36
9	Nitromethane	3-Pentanone	101.2	102.05	99.1	0.633	20.9	22.1	0.16	0.34
10	Nitromethane	Ethyl Propanoate	101.2	99.1	96.0	0.474	22.0	22.1	0.31	0.42
11	Nitromethane	Methyl Butanoate	101.2	102.65	97.95	0.627	21.7	22.1	0.26	0.52
12	Nitromethane	Propyl Ethanoate	101.2	101.6	97.6	0.578	21.9	22.1	0.26	0.45
13	1,2-Benzendiol	1,4-Dibromobenzene	245.9	220.25	218.15	0.192	(21.3)	(22.5)	1.21	0.96
14	1,2-Benzendiol	1-Chloronaphthalene	245.9	262.7	241.0	0.680	(21.3)	(22.5)	1.00	1.08

In the above classifications all ε's in each type of solution of course involve more or less attractive energy due to dispersion effect.

So far we have considered the azeotropic mixtures on the basis of the fairly simple model proposed. Apparently it is not satisfactory for quantitative discussions, since the values of w_1 and w_2 calculated from equations (19) and (20), respectively, do not agree so well with each other, though they show rough coincidences. The cause of considerable disagreements in No. 1 and 6 of Table I is uncertain and will be left to further study. It is mentioned, however, that this disagreement may be partly due to the approximation we used on the one hand and to the errors introduced in experimental data on the other hand. In the class (d) solution such a disagreement is remarkable and in most cases $w_1 < w_2$. This will give a measure of the deviation of activity coefficients from regular solutions.

It is of great interest to see how w's change with varying pairs of component molecules in connection with the azeotrope-forming power of solutions. In general the decreasing order of azeotrope-forming power is (c), (d), (a) in minimum type azeotropes.

Summary

The general expression for the azeotrope-forming power of binary solution has been derived and the conditions for azeotrope existence presented. The quasi-crystalline model has been adopted for the solution, which is assumed to be a strictly regular solution at an azetropic point and an explicit representation for interaction energy of component molecules introduced.

Azeotropic mixtures have been grouped into four classes according to the type of molecular interaction and the azeotrope-forming power (molecular interchange energy) has been calculated and discussed.

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An Anomalous Catalytic Activity of Reduced Silver

By Kozo HIROTA and Yasushi KOBAYASHI

(Received August 3, 1956)

Introduction

Though metallic silver is often used an oxidation catalyst, its activity does not seem clarified yet in spite of its simple structure as compared to that of defect catalysts. In the course of our study[1,2] on the isotopic exchange reaction between heavy oxygen and carbon dioxide, $O^*_{ads.} + CO_2 \rightleftarrows O_{ads.} + COO^*$, we were obliged to conclude that even when the silver catalyst is reduced at 300°C for five hours before each run, there remain some chemical species containing oxygen which can exchange with the gaseous one. As the experiment was carried out under the partial pressure of oxygen of about 70 mmHg, the formation of silver oxide is improbable from the view point of thermodynamics[3]. On the other hand, as the exchangeable oxygen was found to exist in so great an amount that it is of comparable order of magnitude to that which was monomolecularly adsorbed[4], it was presumed that they may remain as an occluded state in the layers very close to the surface (subsurface) rather than as the adsorbed state on the surface. Both sorts of oxygen-containing species may probably be oxygen atoms, as assumed in the present paper and also by other researchers[5,6] in which, however, only the adsorbed state was considered.

The present research was begun in order to support the above presumption with experimental facts, studying the behaviour of oxygen adsorbed by the silver catalyst in detail, with special regard to the method of reduction of the catalyst. To meet the object, the exchange reaction between adsorbed oxygen and carbon dioxide was utilized as well as the reaction between adsorbed oxygen and carbon monoxide, $O_{ads.} + CO \longrightarrow CO_2$, which can easily occur even at room temperature[5].

Experimental

The catalyst (10.0 g.) was newly prepared by reducing the silver oxide with a flow of hydrogen gas at 300°C, similarly as in the previous reports[1,2]. Preparation of the silver oxide was different only in the procedure that, instead of ammonium hydroxide, it was precipitated by barium hydroxide as done Benton et al.[7]. The precipitated silver oxide was washed with distilled water free from carbon dioxide, until no barium ion was detected in the filtrate. It was found that this catalyst has a normal lattice distance 4.086 Å, as compared to the values in the tables*. The catalyst was reduced again in each run before the experiments at 250°C or 275°C to minimize the possible sintering of the catalyst.

The apparatus is shown in Fig. 1, its wall was

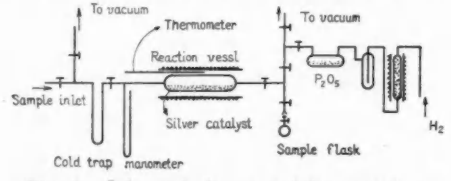

Fig. 1. Schematic diagram of the apparatus

made of hard glass, the reaction tube was 119 ±1 cc. (NTP) and the catalyst was spread on the wall of the tube a few millimeters in thickness. The temperature of the furnace was kept constant within ±1°C for a few hours and within ±5°C for a few days by the use of an automatic controlling device.

The heavy oxygen (OO*) used was prepared in our laboratory by a thermal diffusion column, its molar isotopic concentration being 2.58%. The abundance ratios of OO^*/O_2 and COO^*/CO_2 were determined mass-spectrometrically. The accuracy of one determination of the abundance ratio was ±0.05%.

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* Landolt-Börnstein, 6. Aufl., 4.077s KX (25°C); Natl. Bur. St., 4.086$_2$Å.

TABLE I

EXPERIMENTAL RESULTS (Reaction Temperature: 200°C)

No. of Runs	Time of the 1st Outgassing (hr.)	Press. before the Reduction (mmHg)	Reduction Time (hr.)	Time of the 2nd Outgassing (hr.)	Initial Gas and Press. (mmHg)	OO*, CO* or COO* % in the Gas	OO* or COO* % in Gas after the Reaction (Time in hr.)		
I.	Experiment I			(Reduction Temperature 250°C)					
1	—	$\sim 10^{-3}$	8	4	O_2 76	2.58	2.36 (1/3)	2.08 (1)	1.82 (25)
2	3	2×10^{-4}	10	5	O_2 82	2.58	2.58 (0.5)	2.44 (16.5)	
3	5.5	1×10^{-4}	18	4	CO_2 24	0.40	0.92 (3)	—	
4	3.5	5×10^{-5}	40(7)	4	O_2 73	2.58	—	2.41 (18)	
II.	Experiment II			(Reduction Temperature: 275°C)					
5	5.5	1×10^{-5}	65(16)	6	O_2 61	2.58	2.58 (3)	2.46 (18)	
6	4	3×10^{-5}	—	—	CO_2 29	0.40	0.87 (3)	0.98 (20)	
7	24	$\sim 10^{-4}$	18(3)	4	O_2 91	2.58	2.58 (3)	2.48 (44)	
8	5	$\sim 10^{-5}$	18(3)	5	CO_2 70	0.40	0.46 (3)	0.43 (19)	
9	4	$\sim 10^{-5}$	18.5(3)	5.5	CO 58	0.20	0.20 (3)	0.20 (20)	
10	5	$\sim 10^{-5}$	18(3)	5	O_2 50	0.40	0.68 (3)	0.92 (20)	

N. B.
Pressure of the second outgassing need not be described, because it reached to 10^{-6} mmHg within a few minutes. The first outgassing of No. 5 was carried out at 250°C. Numerals in parentheses in the fourth column designate the time of reduction by flowing hydrogen gas.

Results

All the experiment which is shown in Table I was performed, in the order of the number of runs, and can be divided into I and II.

The first experiment (I) was done, in order to confirm the conclusion reported already that some chemical species containing oxygen atoms remain in the catalyst even after the reduction by hydrogen. Hereafter this sort of oxygen will be called the residual oxygen, the existence of which was really shown by the reduction at 250°C, as will be described.

By the decrease of concentration of heavy oxygen in the gas (No. 1) eight hours' contact of hydrogen was insufficient to remove all the residual oxygen, while by the repeated treatment of heavy oxygen these kinds of oxygen were fairly replaced by the heavy ones (No. 2). This catalyst was then treated by normal carbon dioxide in the next run (No. 3), by which the possible exchange effect with heavy oxygen charged in the catalyst was observed. The dilution of the heavy oxygen which ought to be brought about by this procedure was confirmed by the next run (No. 4). In this run, notwithstanding the fact that the catalyst was reduced for forty hours, for seven of which hydrogen gas was allowed to flow over the catalyst the decrease of heavy oxygen concentration was observed to the degree equivalent to the dilution which occurred in No. 3. It seems that because of the process of severer reduction, the object, to charge the catalyst with heavy oxygen, was practically attained by only one run.

As the existence of oxygen in the catalyst even after the reduction at 250°C was shown by the above experiment, the second experiment (II) was carried out, in order to investigate its nature in detial, i.e., presumption in the former report. In the present series of runs, the reduction and degassing temperatures were raised from 250°C to 275°C, so as to remove the oxygen occluded as much as possible.

In the run next to No. 4, heavy oxygen was again diluted (No. 5), when it was brought into contact with the catalyst, probably because of a severer condition than in Exp. I. Then if the catalyst was only degassed and not reduced before the introduction of carbon dioxide, the exchange effect was observed as in No. 3, suggesting that exchangeable oxygen remains on the surface (No. 6). However, if the catalyst was reduced (No. 7) and was again brought into contact with carbon dioxide (No. 8), it seemed that the above oxygen had been removed, because in this run, the isotopic composition of the carbon dioxide did not change practically. Moreover, it was found in No. 9 that carbon monoxide neither exchanges nor reacts with the residual oxygen as shown by the constancy of its isotopic composition and its pressure. However, the possible suspicion that heavy oxygen might already be removed completely was rejected by making normal oxygen contact with the catalyst (No. 10); i.e., heavy oxygen still remained in the catalyst after the

repeated reduction process before the commencement of three runs (No. 8, 9 and 10).

Discussion

Now, the above result will be discussed in more details. First, if it is assumed that the concentration of the residual oxygen in the catalyst is 2.48% (No. 7) and that an equilibrium is realized between normal oxygen and the residual heavy oxygen after twenty hours of contact (No. 10), giving 0.92% as the concentration of the latter, the total amount of oxygen per gram-catalyst remaining in the catalyst, if expressed by gaseous volume (NTP), will be given by

$$69\,\text{cc.}\times\frac{0.92-0.40}{2.48-0.92}\times\frac{50(\text{cm.})}{760(\text{cm.})\times 10.0\,\text{g.}}$$
$$=0.15_1\ \text{cc./g.-cat.} \qquad (A)$$

considering that the gaseous volume in the tube at 200°C corresponds to 69 cc. (=119 ×273/473) at NTP, and neglecting the effect of isotopic separation.

According to our adsorption measurement[4], the amount of oxygen monomolecularly adsorbed on the surface is 0.069 cc./g.-catalyst at 200°C, so the numeral obtained in (A) is twice as large as the present one. Second, by the similar reasoning as the above, the volume (NTP) of oxygen remaining after the evacuation will be estimated by the data of No. 6 and 7 as follows:

$$69\,\text{cc.}\times\frac{0.98-0.40}{2.48-0.98}\times\frac{29(\text{cm.})}{760(\text{cm.})\times 10.0\,\text{g.}}$$
$$=0.10_2\ \text{cc./g.-cat.} \qquad (B)$$

It is found that the amount of exchangeable oxygen is smaller in this case but larger than that absorbed on the surface, suggesting that most of the exchange reaction seems to proceed between the normally adsorbed oxygen and carbon dioxide.

Thus it is made clear that metallic silver, though easily reducible, retains oxygen atoms firmly even when the reduction was performed carefully. Though the existence of non-removable oxygen was already reported by Benton and Bell[3], it can be shown by the present investigation that such oxygen in the catalyst is not restricted to one kind of state. It may exist as an adsorbed state on the surface, but also as a state more firmly bound, e.g., in the subsurface rather than to the adsorption to a special part of the surface. Because, by the curious behavior shown in No. 8, 9 and 10, most firmly bound oxygen ("residual oxygen") can neither exchange with carbon dioxide nor react with carbon monoxide, but, contrary to our expectation, it can exchange with gaseous oxygen.

The above behaviour can be explained analogously by the scheme proposed by Garner et al.[8], in the case when cuprous oxide is in contact with oxygen; i.e., when oxygen is brought into contact with the silver surface, silver atoms on the surface will migrate so as to cover some of the oxygen atoms, and the oxygen atoms thus covered will exchange with the residual oxygen atoms. On the other hand, as both carbon dioxide and carbon monoxide are slightly adsorbed to silver, probably to such a degree as one-hundredth of oxygen[4] even if they are adsorbed such migration cannot occur in case of contact with these gases. It is natural, therefore, that the exchange reaction was not observed in No. 8 and 9. However, the process of migration will not continue infinitely into the silver bulk-phase, as can be expected for the thermodynamical reason. This is actually realized by the fact that the amount of adsorbed oxygen remains to the degree, corresponding to one or two layers. However, as the isotopic effect in adsorption equilibrium is not taken into consideration the quantitative discussion on this matter will not be developed further.

Conclusion

From the different catalytic behaviour of reduced silver against carbon dioxide, carbon monoxide and oxygen, it may be concluded that the silver retains a special kind of "residual oxygen" firmly after it is brought into contact with oxygen, even at above the temperature region, at which the dissociation of silver oxide would begin.

A part of the expense for the experiment has been defrayed from a grant given by the Ministry of Education, to which the author's thanks are due.

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SHORT COMMUNICATIONS

An X-ray Study on Thiacyclohexane

By Seiichi KONDO

(Received June 18, 1956)

McCullough and his collaborators[1] reported that thiacyclohexane (pentamethylene sulphide) has three modifications in the solid state and the molal entropy of fusion is 2.002 cal./deg. A chair form having the point group symmetry Cs is suggested for the molecule from the infrared and Raman spectroscopy.

The highest temperature modification of this crystal, stable between the transition point, 240.02°K, and the melting point, 292.25°K, is found to be optically isotropic and shows plastic behavior. These facts, together with the very low value of molal entropy of fusion, suggest that this modification falls into the category of plastic crystal.

The dipole moment of this molecule is estimated to be about 1.7 D.U., assuming the bond moment of C–S to be 1.4 D.U., (obtained from the dipole moments of diethyl and diphenyl sulphides[2,3]), and the valence angle C–S–C, 105°[1,4]. It is of interest to see that the physical properties of this compound in the highest temperature modification such as the entropy of fusion, plasticity and isotropy are quite similar to those of the non-polar compound cyclohexane[5], in spite of the difference in the molecular symmetry and polarity, which would give rise to different types of intermolecular correlation in the solid state. Furthermore, another related compound pentamethylene oxide having the molecular form analogous to that of thiacyclohexane does not seem to give plastic crystals. It would be because of the difference between the electronegativity of oxygen and sulphur atoms. The highest temperature modification has been studied by means of X-rays.

(A) The material used for this investigation was prepared and purified by the American Petroleum Institute research project 48 at the Laramie Station of U.S. Bureau of Mines, Wyoming. The material received was claimed to be 99.92% pure. It was again purified by drying and sublimation and was sealed in a thin wall capillary made of borosilicate glass. Single crystals can be grown very easily in a capillary by slow cooling of the melt. It is likely to occur that the [110] direction of the crystal lies nearly parallel to the capillary axis.

Laue, rotation, and oscilation photographs were taken with filtered Cu Kα and Mo Kα X-rays, at 14°C.

(B) The symmetry of the crystal is determined as face centered cubic with four molecules in the unit cell. The six Bragg reflection spectra observed are indexed as 111, 200, 220, 311, 222 and 331. The lattice constant is found to be 8.69±0.02 A at 14°C. With this value, the density of the crystal is calculated to be 1.036, which seems to be reasonable compared with the measured value, 0.985, of the liquid at 21°C. The spectral intensities are much like those of other plastic crystals such as trimethylacetic acid[6].

Considered from the standpont of the crystal and molecular symmetry, molecules will be in highly disordered orientation, including some sort of rotational motion, keeping presumably the center of the mass of the molecule fixed at the lattice site. We have observed very pronounced X-ray diffuse scattering. Spot-like diffuse scattering is appearing on Laue photographs, the intensity of which is strongest around the reciprocal lattice points 200 and 111, and there are also weaker ones around 100. The general appearance of those diffuse scatterings are very similar to those of other plastic crystals like cyclohexane[5].

From these observations we conclude that the highest temperature modification of thiacyclohexane belongs to the plastic crystal.

The author is very grateful to Professor Tsutomu Oda for his valuable discussions and to Dr. J.P. McCullough of the Thermodynamic Laboratory, Bartlesville, Ohio, of U.S. Bureau of Mines for the supply of the material and useful discussions.

Laboratory of Physical Chemistry, Osaka University of Liberal Arts and Education

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Additions and Corrections

Volume 28, 1955

T. Ishikawa: Note on the Constancy of ε in the New Equation of State.

Page 90. In col. 1, the first line, for "$b=v_c/3$" read "$b=V_c/3$".

T. Ishikawa: Some Remarks on the New Equation of State as Applied to the Critical Region.

Page 515. In col. 1, line 10, for "$(\partial^3 p/\partial v^3)_{T=T_c}=0$" read "$(\partial^3 p/\partial v^3)_{T=T_c}\neq 0$".

H. Inokuchi: The Effect of Pressures on the Semi-conductivity of Isoviolanthrone.

Page 571. In Fig. 3, the abscissa scale, for "kg/cm²" read "ton/cm²".

F. Egami, T. Asahi, N. Takahashi, S. Suzuki, S. Shikata and K. Nisizawa: Chemical Studies on Charoninsulfuric Acid.

Page 685. In col. 2, lines 4 to 6 from the bottom (*lampas*.....that it) should be transferred between lines 1 and 2 from the bottom in the same column.

Additions and Corrections

Volume 29, 1956

T. Sasaki and M. Muramatsu: The State of Metal Ion in Aqueous Solutions and its Surface Chemical Effect. II.

Page 36. In col. 2, line 5 from the bottom, for "wettign" read "wetting".

Page 37. In Table I, in col. 5, for "90.24" read "0.249".

M. Nakagaki and A. Shimazaki: Colloid Chemical Studies on Starching Materials. 1.

Page 61. In col. 1, line 10 from the bottom, for "η_N" read "η", for "distroyed" read "destwyed" and line 17 from the bottom, for "Hg-sulfosalicylate-sal" read "Hg-sulfosalicylate-sol".

Page 62. In col. 2, line 5 from the bottom, for "90 C" read "90°C".

Page 63. In col. 1, line 11, for "greter" read "greater" and line 6 from the bottom, for "season" read "reason". In col. 2, line 15 from the bottom for "polymerization, degree" read "polymerization degree,".

M. Nakagaki and S. Iida: Behavior of Surface Active Molecules at Interface I.

Page 64. In col. 2, line 4, for "Let the fraction of" read "Let the fraction" and line 8, for "hydrocarbon chain chain" read "hydrocarbon chain".

Page 65. In col. 1, line 16, insert the following paragraph between the words "pressure" and "is" "to extend the film, and the difference of these two pressures". In the same column, line 5, for "small" read "smaller". In col. 2, Equation (14) should read "$\xi=\dfrac{A-A_P}{A_P-A_H}=\dfrac{A-A_P}{B}$"

Page 67. In col. 1, line 4, for "at" read "as". In col. 2, lines 18 and 22, for "Anam" read "Adam". In Table I, in the title, for "A_P ω" read "A_P and ω" and in col. 1, for "Choresterterol" read "Choresterol".

Page 68. In Table II, in col. 5 for "31.2" read "21.2". In col. 2, line 9 from the bottom, for "autors" read "authors". In col. 2, line 6 from the bottom, for "closs" read "cross".

K. Aoki and J. Hori: Interaction between surface active agents and proteins. I.

In this paper, exchange the figure 1 for 7.

T. Tokuda: Atomic weight of Oxygen in Quanty of Contrasted Geolozic Origin.

Page 189. In col. 2, line 3 from the bottom, for "froat" read "float".

Page 191. In col. 1, line 23, for "Dork" read "Doak".

M. Nakagaki: Physico-Chemical Studies on Dyeing Process. I

Page 201. In col. 2, line 5 from the bottom, for "diss cuss than the interation" read "discuss the interaction".

Page 202. In col. 2, line 5 from the bottom, for "from " read "From".

Page 203. In col. 1. the first line, for "varification" read "verification".

Page 204. In col. 1. line 11 from the bottom, for "known, yet" read "known yet,".

M. Fujimoto: Über die unmittelbare Messung von den Zuständen in die Ionenaustausch-herzphase adsorbierter Komplexionen mit den Harzmembranen.

Page 285. In vol. 2, the first line of the paper, for "Whnn" read "Wenn".

Page 286. In col. 1, line 2, for "einbacheV ergleichung" read "einbache Vergleichung".

Page 287. In foot note, line 4 from the bottom, for "Absorptionsbäuder" read "Absorptions bänder".

M. Takebayashi and Y. Ito: Copolymerization of Optically Active Ethyl-2-methyl-2-ethyl-2-butenoate with Vinyl Acetate.

Page 287. In the subject and col. 2, line 3, for "2-Methyl-2-ethyl-2-butenoate" read "2-Methyl-2-ethyl-3-butenoate".

M. Fujimoto: Mikroanalyse mit Hilfe von Ionenaustauschharzen. V.

Page 597. In col. 2, the last line, for "werden[6]" read "werden[8],"

M. Fujimoto: Mikroanalyse mit Hilfe von Ionenaustauschharzen. VI.

Page 603. In col. 2, the last line, for "ein Stunde" read "eine Stunde".

Page 604. In col. 1, line 2, for "Vekuumexikkato:" read "Vakuumexikkator".

T. Kanzawa: Studies on the Infrared Spectra of Ephedrine and Related Compounds. III.

Page 665. Exchange the figure 1 for 2.

H. Onishi: Notes on the Geochemistry of Germanium. In this paper, for all of "ppm." read "p. p. m.".